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"PREPARATION AND CATALYTIC ACTIVITY OF SUPPORTED
GROUP VB AND VIB METAL CLUSTERS"

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"PREPARATION AND CATALYTIC ACTIVITY OF SUPPORTED
GROUP VB AND VIB METAL CLUSTERS"

EXECUTIVE SUMMARY

The Report is divided into five chapters. In the first, introductory chapter a review of existing literature on Group VB and VIB Metal Clusters is given, indicating the scope of the project. Clusters are defined as molecular species containing more than one metal atom, and larger clusters have been compared and contrasted to metal fragments. The interest in clusters from a catalytic viewpoint is that they afford the opportunity of studying well defined site geometry, if they remain intact when anchored to a support surface. Of the multitude of known clusters of metals in the Groups VB (V, Nb, Ta) and VIB (Cr, Mo, W) a few representative ones were selected for study. These can be divided into three groups, based on their content of three (Group 1), four (Group 2) or 6 (Group 3) metal atoms respectively. In practice the element molybdenum was chosen for the larger part of the study because of its proven value in industrial catalysts for hydrocarbon processes. For control purposes the pi-allyl complexes $\text{Mo}(\pi\text{-C}_3\text{H}_5)_4$ and $\text{Mo}_2(\mu\text{-C}_3\text{H}_5)_4$ were made and anchored on $\gamma\text{-Al}_2\text{O}_3$ as previously reported in the literature. Conventional Co-Mo/ Al_2O_3 catalysts were also selected for comparison purposes.

In Chapter Two the preparation of the control species and the series of new supported clusters is described. They were characterized by infrared and Raman spectroscopy, electronic spectroscopy (uv-visible) and differential scanning calorimetry was used to determine their thermal stability. These measurements were applied to the pure cluster compounds, and to the materials obtained after anchoring of the complexes to $\gamma\text{-Al}_2\text{O}_3$ and fluorided $\gamma\text{-Al}_2\text{O}_3$ supports.

As an extension of the work, Nb_6 and Ta_6 clusters (of general formula M_6Cl_{14}) were prepared and intercalated into the clay mineral Montmorillonite to produce so-called "pillared clays". These materials had been reported in the literature but no studies of their possible catalytic activity had been made.

The potential catalysts, synthesized as above, were then tested on model compounds (cumene hydrocracking, thiophene hydrodesulphurization, propene hydrogenation) and the more successful materials were then used in hydrotreating of Syncrude Coker Gas Oil, after sulphidation. After the procedural descriptions in Chapter Two, the actual results are tabulated in Chapter Three, and discussed in Chapter Four.

Of the molybdenum clusters prepared and studied, the Mo_6 species contained in $(H_3O^+)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ was catalytically much more active than any other. The key results on model compound testing are given in Table 3.9. Promotion of the molybdenum by cobalt, and addition of fluoride to the Al_2O_3 support, both influenced the catalytic performance of those materials in the selected reactions. When used in the hydrotreating of Syncrude Coker Gas Oil in a stirred batch reactor these catalysts gave results (Table 3.10) comparable with those from conventional hydrotreating catalysts, but with a much lower loading of molybdenum. Of particular interest is the result from Cat-33, which contained Co and F^- in addition to the Mo_6 additive. The aromaticity of the produced liquid was 0.18 suggesting that catalytic conversion of aromatics to naphthenes or cracked naphthenes was significantly higher than for any other catalyst studied.

In Chapter Five a brief discussion is given of the possible experiments which should be undertaken to pursue this research further. Belated attempts by Dr. Jasim to fill in some of the obvious gaps met with an unexpected obstacle. A slight change in preparative procedures, employing HCl as a solubilizing agent for the clusters, rendered the resulting supported clusters catalytically inactive in the test reactions.

"PREPARATION ET ACTIVITE CATALYTIQUE D'AGREGATS METALLIQUE
SUPPORTES DU GROUPES VB ET VIB"

RESUME EXECUTIF

Ce rapport est divisé en cinq chapitre. Dans le premier chapitre, qui sert d'introduction, on retrouve un résumé de l'activité littéraire déjà existante sur les agrégats métalliques des groupes VB et VIB, ce qui nous donne une idée de la portée du projet. Les agrégats sont défini comme étant une espèce moléculaire contenant plus d'un atome métallique, et les plus grands agrégats ont été comparés et différenciés des fragments métallique. Du point de vue catalytique, les agrégats sont intéressant puisqu'ils offrent une chance d'étudier des sites possédant une géométrie bien définie, si ceux-ci demeurent intacts lorsqu'ils sont encrés à la surface supportrice. Parmi la multitude d'agégats métallique connus des groupes VB, (V, Nb, Ta) et VIB (Cr, Mo, W), quelques représentants de ceux-ci furent choisis pour cette étude. Ceux-ci peuvent être divisé en 3 groupes d'après le nombre d'atome métallique qu'ils contiennent: trois pour le groupe 1, quatre pour le group 2 et six atomes pour le groupe 3. En pratique, le Molybdène a été choisi pour la majeur partie de l'étude, à cause de son utilité comme catalyseur industriel pour les processus d'hydrocarbures. Pour des fins de controle, des complexes de pi-allyl $\text{Mo}(\pi\text{-C}_3\text{H}_5)_4$ et $\text{Mo}_2(\mu\text{-C}_3\text{H}_5)_4$ ont été formés et encrés sur $\gamma\text{-Al}_2\text{O}_3$, tel que déjà décrit dans la littérature. Des catalyseurs conventionnel de $\text{Co-Mo/Al}_2\text{O}_3$ ont aussi été choisi pour fin de comparaison.

Dans le deuxiemè chapitre, on retrouve une description de la préparation des espèces de controle et de la série de nouveau agrégats supportés. Ils ont été caractérisés par spectroscopie infrarouge et Raman, spectrsco pie

électronique (UV-visible) et la calorimétrie différentielle en mode de balayage a été utilisé pour définir leur stabilité thermique. Ces mesurage ont été effectués sur les agrégats purs, et sur les produits obtenus après l'encrage des complexes sur des supports de $\gamma\text{-Al}_2\text{O}_3$ et $\gamma\text{-Al}_2\text{O}_3$ fluoré.

En continuation de ce travail, des agrégats de Nb_6 et Ta_6 (de formule générale M_6Cl_{14}) ont été préparés et intercalés dans de l'argile minérale Montmorillonite pour produire des "argile end pilier". Ces matériaux ont été décrits dans la littérature, mais aucune étude d'une quelconque activité catalytique n'a été entreprise.

Les catalyseurs synthétisés de la manière décrites précédemment furent testé sur des composés types (hydrocraquage du cumène, hydrodesulfurisation du thiophène, hydrogénation du propène), et les catalyseurs les plus prometteurs ont ensuite été utilisé pour l'hydro-traitement du gas-oil de craqueur de Syncrude ("Syncrude Craker Gas Oil") après sulfidation. Après la description de la méthode expérimentale dans le chapitre 2, les résultats sont tabulé dans le chapitre 3, et discuté dans le chapitre 4.

Parmi les agrégats de molybdène préparés et étudiés, les espèces de Mo_6 contenu dans $(\text{H}_3\text{O})^+[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$ furent catalytiquement beaucoup plus actives que tout autres. Les résultats clés sur les test avec les composés types sont donnés dans le tableau 3.9. La promotion du molybdène avec du cobalt, et l'addition de fluorure au support de Al_2O_3 ont influencé la performance catalytique de ces matériaux dans les réactions choisies. Lorsque utilisé pour l'hydro-traitement du gas-oil de Syncrude dans un réacteur à charge sous agitation, ces catalyseurs produisirent des résultats (tableau 3.10) comparable à ceux obtenu pour des catalyseurs conventionnels d'hydro-traitement, mais avec un chargement bien moindre du molybdène. Notons spécialement les résultats obtenus pour Cat-33, qui contenait Co et F^- en

plus de l'additif Mo_6 . L'aromaticité du liquide obtenu fut de 0.18, ce qui suggère que la conversion catalytique des aromatiques en naphthènes ou naphthènes craqués est nettement plus élevée que pour tout autre catalyseur étudié.

Dans le chapitre cinq, on retrouve une brève discussion des expériences possible qui devraient être entreprises pour poursuivre cette étude plus à fond. Des efforts tardifs de la part du Dr. Jasmin pour remplir certaines lacunes évidentes furent arrêtés par un obstacle imprévu. Un léger changement dans la méthode de préparation, l'utilisation de HCl comme agent solubilisant des agrégats, rendit les agrégats supportés obtenu catalytiquement inactif dans les réactions types.

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Introduction

This report is presented to the Department of Energy, Mines and Resources, Canada, in fulfillment of the contract #05785-00317 between the Department of Supply and Services, Canada, and the University of Calgary.

The objectives of the project were to:

- (a) Review existing literature on clusters of Group VB and VIB metals.
- (b) Prepare selected supported metal clusters and then to test their catalytic activity in model compounds reactions.
- (c) Take the most promising examples and test them as catalysts for the hydrotreating of a heavy gas oil.

The work was supervised by Drs. Kydd and Boorman of the Department of Chemistry, University of Calgary, but carried out by a research associate, Dr. Khalid S. Jasim. Subsequent to the completion of the project Dr. Jasim accepted a professional position with Domtar Inc., in Montreal. His experience of working on this project was clearly an asset in the job market. An extension to the project, involving preparation of pillared clays was carried out by an undergraduate summer student, Mr. J. Padda.

Chapter 1

A Review and Evaluation of Existing Literature
on Group VB and VIB Metal Clusters

1.1 Heterogeneous and Homogeneous Catalysis

A catalyst may generally be defined as a substance that increases the rate at which a chemical reaction reaches equilibrium (1). However, a catalyst introduced into a reaction system is more accurately described as a catalyst precursor due to the fact that the active catalytic entities are possibly produced under the reaction conditions (2). Catalysts are conventionally classified as heterogeneous and homogeneous. It is important to compare the advantages and disadvantages of both classes. From Table 1.1, it is obvious that there are some advantages of the homogeneous catalysts: (a) because there is no surface effect on the activity, homogeneous catalysts are more effective and more specific than heterogeneous ones; (b) the former can be made more reproducible; (c) they have fixed stoichiometry and structure; (d) they have high capability of modifications; (e) they work under milder conditions; (f) the consistency of homogeneously-catalysed reactions can be maintained better over a longer reaction time and the catalysts requirement are practically minimal (3,4); and (g) the depth of understanding of such reactions is more advanced than their heterogeneously-catalysed counterparts, simply because the former are more selective and therefore kinetically and mechanistically more accessible, they are fairly easily studied spectroscopically by IR, Raman, UV/vis, NMR, ESR, Mössbauer spectroscopy and magnetic susceptibility etc., even under actual reaction conditions. Their disadvantages are: (a) the contact separation, which is one of the central problems in the technical applications. It may be achieved by distillation, solvent extraction, chromatography, chemical decomposition with subsequent filtration, etc.; (b) industrially, the above operations are not quantitative,

Table 1.1. Comparison of Homogeneous and Heterogeneous Catalysts.

No.	Property	Homogeneous	Heterogeneous
1.	Form	Soluble Transition Metal Complexes	Supported or Suspension Metals, Metal Oxides or Metal Complexes
2.	Phase	Liquid or Gas	Gas/Solid
3.	Activity	Low	High
4.	Selectivity	High	Low
5.	Active Centers	All Metal Atoms	Surface Atoms Only
6.	Concentration	Small	High
7.	Diffusion Problems	Not Present	Present
8.	Structure	Known	Indefinite
9.	Stoichiometry	Known	Indefinite
10.	Modification Possibility	High	Small
11.	Reaction Conditions	Mild	Severe
12.	Catalyst Separation	Costly	Easy

therefore total removal of the catalyst necessitates additional purification, which is costly; (c) the presence of small amounts of catalyst in the system makes its separation and re-use additionally difficult. A great deal of care is required to avoid losses since often expensive chemicals are used.

On the other hand, heterogeneous catalysts comprising metals, metal oxides, metal sulfides or metal complexes are usually dispersed on inorganic oxide supports to increase the effective surface area per gram of metal component and to dilute the catalyst for better temperature control. Their advantages (5) are: (a) high thermal and mechanical stability, (i.e. robustness); (b) high activity for a wide range of reactions; (c) ease of separation of products from catalyst and reactants; and (d) capacity for use in packed and fluidized bed reactors depending on the particle size. However, it is generally difficult to prepare reproducible and catalytically active molecular structures with well-defined properties on ill-defined heterogeneous surfaces of inorganic oxides. Therefore, the disadvantages of conventionally prepared catalysts are: (a) design, modification, improvement and reproducibility limits, frequently due to undefined structure and stoichiometry of the active sites; (b) limited accessibility and effectiveness of the catalytic component due to the fact that only surface atoms involve in the catalytic reactions; and (c) severe and costly reaction conditions.

Although much attention has been paid to the preparation and design of solid conventional catalysts with high activities and selectivities, and to the determination of the essential factors which influence the catalytic process such as surface structure, the environment and the oxidation state(s) of the active sites (6-9) using state-of-the-arts instruments and techniques, these major parameters remain unresolved, probably due to the high hetero-

geneity of the prepared catalyst surfaces which restricts the molecular level research on the kinetics, mechanism and origin of the catalytic activities.

From the above discussion, it is apparent that although the high selectivity and specificity often observed with homogeneous catalysis have obvious potential in large scale catalytic processes, the use of such catalysts presents technical difficulties. However, such problems have stimulated considerable interests in the study and development of homogeneous catalysts in a supported form (10-22). The development of this kind of catalyst is of great practical importance. Problems often associated with homogeneous catalysts (separation of catalyst from reaction medium, corrosion of reactors and low solubility of catalysts) can be minimized whilst retaining the desired properties (high activities, selectivities and reproducibility of action). Tailored metallic catalysts with well-characterized active sites provide valuable information on reaction mechanism and factors affecting the origin of catalysis as well as a new implication for preparation of novel and efficient solid catalysts. The majority of these heterogenized homogeneous catalysts (i.e. hybrid catalysts) are metal carbonyls (23,24). However a number of organometallic compounds containing π -allyl and π -methallyl have been supported on inorganic oxides and their surface and catalytic behaviours studied. The work of Yermakov (25) and Iwasawa (26-35) requires particular attention. Synthesis of heterogenized homogeneous catalysts involving inorganic matrices have all utilized preconditioned inorganic oxides in highly porous granular form (16,17). Generally, alumina and silica have been used for these purposes. However, enzymes have been heterogenized on porous glass and oxide-coated metals (36). Inorganic supports have reactive surface hydroxyl groups. Common practice involves their reaction with organochloro-

silanes which either contain the desired functional group or can be subjected to later modification (37). However, other reactions can be used to functionalize alumina and/or silica with phosphines (37), amines (38), thiols (38), hydroxamic acid and imidazoles (39) and some other less common functional groups (20). Accordingly, the distance along the organic fragment linking the surface of the alumina or silica and the functional group can be controlled. This distance is critical to the catalyst performance (36).

There are three essential techniques to bond metal complexes to functionalized matrices: (a) ion exchange for charged complexes (17,40-42); (b) ligand displacement for neutral complexes (17,40,41); and (c) bridge splitting (43). In addition, grafting of a metal complex, which has a reactive metal-carbon bond, with the OH groups of the inorganic oxide surface is also possible (44).

However, components of the supported catalyst system must each be tailored to the reaction requirement. To enhance catalytic activity, it may be preferable to anchor the metal complex to the support through a chemical chain (anchoring) rather than bonding it directly to the support system (grafting) (45), because catalysts with short links along the organic chain between the functional group and the support surface are of lower activity than those with long links. Such a phenomenon also occurs with heterogenized enzymes (36).

Catalysts prepared from the interaction of organometallic compounds and oxide supports can be used directly for catalytic reactions. However, because of the possibility of elimination and substitution reactions involving the organic ligands, the surface complexes in these types of catalysts may serve as starting materials for the preparation of surface compounds of

other compositions. The reductive elimination of the organic ligands may be utilized to prepare low-valent ions of transition metals on the surface of the catalysts. Oxidation or reduction of surface organometallic compounds may be used to synthesize surface compounds containing transition metals in the highest and lowest oxidation states respectively. Thus surface organometallic compounds may serve as excellent precursors for obtaining supported transition metal ions in various oxidation states. However, interesting trends in the direction of future activity in this area of research are:

- (a) the study of the influence of the ligand environment of surface transition metal complexes on the catalytic activity, which might involve:
 - (i) surface hydroxyl groups may be changed by functionalization.
 - (ii) outer ligands may be removed or substituted.
- (b) reductive elimination of the ligands of surface transition metal complexes may yield a significant concentration of metallic ions in oxidation states which are difficult to obtain by other methods.
- (c) the study of the catalytic properties of mixed metal catalysts, reduction of which may lead to the formation of metal clusters.

1.2 Catalysis by Supported Metal Clusters

Muetterties and Krause (2) classified dinuclear metal complexes with a metal-to-metal bond as clusters. However, in this review, only compounds containing frameworks of three or more mutually bonded metal atoms or ions are considered clusters. Opportunities to improve reactivity and catalytic properties by variation of ligands are greater with cluster compounds than with mononuclear metal complexes. Thus both chemically and catalytically

interesting possibilities exist for catalysis by supported organometallic, coordinations and inorganic clusters (46) such as:

- (a) selectivity by virtue of their discrete structure.
- (b) neighbouring metal centres of the clusters allow multiple binding of a single substrate resulting in precise control of reactant geometry and consequent rate acceleration, offering opportunities for conversions not possible with mononuclear metal complexes.
- (c) clusters allow binding of different substrates to neighbouring positions.
- (d) heteronuclear metal clusters can be sought with one type of metal specifically chosen to bind to one reactant and the other type to bind to the other substrate.
- (e) catalysts may be designed by choice of ligands.
- (f) fluxionality of ligands bonded to metal clusters permitting substrate to react regardless of their initial binding sites.
- (g) metal cluster frameworks themselves may provide catalytic activity.
- (h) synthetic reproducibility: the structure and thus catalytic activity are reproducible.

Therefore it is important to discover whether particular polynuclear metal complexes possess these properties.

In addition to the decomposition of polynuclear metal carbonyls (23,24) on inorganic oxide supports, these type of catalysts may be prepared by procedures identical to their mononuclear counterparts. However, the catalysts may be classified into two categories (5):

- (a) supported metal clusters, where partial or more likely, complete removal of ligands has occurred (highly dispersed, supported metal catalysts).

(b) supported metal cluster compounds (i.e. heterogenized homogeneous catalysts).

Reactions catalysed by metal clusters are numerous, some examples are listed in Table 1.2.

1.3 Catalysis by Groups VB and VIB Metal Complexes and Clusters

There is very limited information on niobium and tantalum complexes as catalysts. They have been reported as benzene and ethylene hydrogenation catalysts, ethylene hydration catalysts and for a variety of dehydration, isomerization and polymerization reactions (58-62). In addition tantalum pentafluoride, oxide and niobium oxides have been reported in patents for oxidation of organic molecules, oxidative dehydrogenation of olefins and paraffins, decomposition of NO_x , the preparation of pivalacetone (63-69) and the preparation of pentylbenzene from benzene and 2-pentene (70). However, niobium sulfide NbS_2 exhibits hydrodesulfurization properties. Using dibenzothiophene, the products of this catalytic process are biphenyl and cyclohexylbenzene at 300°C and 18 atm (71). Much less information is available on catalysis by Group VB metal clusters. To our knowledge, the only report published to date is the catalytic oxidation of Sn(II) by Fe(III) in aqueous solution in the presence of $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ cluster (72). On the other hand, catalysis by supported Group VIB elements prepared by conventional impregnation methods have been studied extensively and have been the subjects of reviews, monographs and text books. This subject is out of the scope of this review and it will not be considered further. However, Iwasawa *et al.* (26-35) have undertaken a very elegant series of experiments detailing the preparation, characterization and some reactions of "fixed" or chemically

Table 1.2. Reactions Catalysed by Metal Clusters.

No.	Reaction	Reference
1.	Olefin Isomerization	47, 49
2.	Olefin Hydrogenation	48
3.	Acetylene Hydrogenation	49
4.	Alkyne Cyclization to Arenes	50
5.	Water Gas Shift Reaction	51
6.	Hydrogenation of Nitrobenzene to Aniline	49, 52, 53
7.	Synthesis of Polyhydric Alcohols and Derivatives from CO and H ₂	54
8.	Synthesis of Methanol from CO and H ₂	54, 55
9.	Fischer-Tropsch Synthesis	56
10.	Hydroformulation of Alkenes	49, 52, 57
11.	Reduction of CO and Ketones	48

supported $\text{Cr}(\pi\text{-C}_3\text{H}_5)_4$, $\text{Cr}_2(\pi\text{-C}_3\text{H}_5)_4$, $\text{Mo}(\pi\text{-C}_3\text{H}_5)_4$ and $\text{Mo}_2(\pi\text{-C}_3\text{H}_5)_4$ catalysts. Reductive elimination of the allyl groups and subsequent O_2 oxidation resulted in Cr(III) and Mo(VI) oxide catalysts of a more uniform nature than conventionally impregnated catalysts. In all the reactions investigated (oxidation of alcohol and propane, metathesis of olefins and ethylene hydrogenation at low temperature, -73 to 20°C), the "fixed" Mo-catalysts had much higher activities and selectivities than impregnated catalysts. Furthermore, the paired catalyst (prepared from $\text{Mo}_2(\pi\text{-C}_3\text{H}_5)_4$) showed superior activity for ethene hydrogenation than isolated species, as well as superior stability. The molybdenum atoms of the fixed catalysts were in uniform tetrahedral environment with S orbital participation in the low valent paired species while high valent paired structure showed strong interaction between adjacent molybdenum atoms.

Although, there are many up-to-date articles and reviews published in different scientific journals (73-78) detailing the applications of metal clusters in catalysis, no information is available on complexes containing more than two molybdenum or tungsten atoms except for the iso- and heteropolymetallates of these elements (79-81). This is rather unexpected since a large number of tri-, hexa- and, to a lesser extent, tetranuclear metal cluster compounds exist for both Groups VB and VIB elements (see next section).

1.4 Literature Review

Very few complexes of vanadium and chromium are known which contain metal clusters. The complex $\{(\text{C}_5\text{H}_5)\text{V}\}_5 (\mu_3\text{-O})_6$ contains the metal in trigonal bipyramidal geometry with a formal oxidation state of 3.4 (82a,82b). Whereas the complex anions $\text{S}[\text{Cr}(\text{CO})_4]_3^{2-}$ and $\text{S}[\text{Cr}(\text{CO})_5]_3^{2-}$ presumably contain

S-capped triangular metal clusters (83). The compound $\text{Cp}_4\text{Cr}_4\text{O}_4$ contains the cubane-like Cr_4O_4 cluster (82b). However, niobium, tantalum, molybdenum and tungsten form numerous coordination and organometallic compounds containing metal clusters. They may be classified according to the nuclearity of the cluster within each complex as: (a) M_3 ; (b) M_4 ; and (c) M_6 frameworks neglecting complexes of nuclearity higher than six.

1.4.1 Compounds Containing Trinuclear Metal Clusters

The number of complexes containing trinuclear metal clusters is increasing very rapidly. During the past few years many have been synthesized and structurally characterized (84,85). However, according to the simplified classification of Müller and co-workers (84), there are three basic trinuclear triangular structures:

- (a) without a μ_3 -ligand;
- (b) monocapped triangular structure with one μ_3 -ligand;
- (c) bicapped triangular structure with two μ_3 -ligands.

All have three metal-to-metal bonds of order ≤ 1 (i.e. electron poor structures) depending on the average oxidation number of the metal atoms. Since these complexes are electron poor they may easily be attacked by inorganic oxide supports functionalized with strong nucleophilic groups to prepare supported triangular metal cluster catalysts. The formal oxidation numbers of the metal ions in these cluster compounds are usually non-integral. They may be prepared under a variety of reaction conditions with numerous non- π -bonding ligands. The M_3 triangular framework is generally preserved during ligand exchange and redox reactions (86). Generally the number of trinuclear metal cluster compounds of Group VB and VIB prepared to date follows the

sequence Mo>W>Nb>Ta. The cation $[\text{Ta}_3\text{Cl}_6(\eta_6\text{-C}_6\text{Me}_6)_3]^+$ (87,108), contains a Ta_3 triangle with three Ta-Ta bonds and without μ_3 -ligands; therefore it belongs to class (a) above. Similar compounds of niobium have also been reported such as $[\text{Nb}_3\text{X}_6(\eta_6\text{-C}_6\text{Me}_6)_3]^n$; $\text{X} = \text{Cl}$, $n = 1, 2$ and $\text{X} = \text{Br}$, $n = 1$ (87-89). Niobium complexes containing the bicapped triangular metal clusters with two $\mu_3\text{-O}$ ligands (class C above) are also known. These are exemplified by $[\text{Nb}_3\text{O}_2(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{5-}$ (90), $[\text{Nb}_3\text{O}_2(\text{O}_2\text{CC}_6\text{H}_5)_6(\text{C}_4\text{H}_8\text{O})_3][\text{NbOCl}_4(\text{C}_4\text{H}_8\text{O})]$ (91), and the polymeric halides Nb_3X_8 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), the latter show little chemical reactivity due to their nondiscrete cluster core which occurs in a chain-like structure (92,93). The above niobium complex (91), as well as $[\text{Nb}_3\text{O}_2(\text{O}_2\text{CCMe}_3)_6(\text{C}_4\text{H}_8\text{O})_3][\text{B}(\text{C}_6\text{H}_5)_4]$ (91), may be hydrolyzed to neutral species. These compounds are similar to the molybdenum complex $\text{Na}[\text{Mo}_3\text{O}_2(\text{O}_2\text{CCH}_3)_9]$ which hydrolyses to the neutral species $[\text{Mo}_3\text{O}_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})(\text{OH})_2]$ in acid medium (94). Accordingly, it may be possible to "fix" the above Nb and Mo ionic complexes as well as the trinuclear W cluster compound $\text{Cs}[\text{W}_3\text{O}_2(\text{O}_2\text{CCH}_3)_9] \cdot 3\text{H}_2\text{O}$ (95) on acidic supports by hydrolysis.

In the past few years work on molybdenum and tungsten revealed the existence of a large number of complexes containing the trinuclear, triangular metal clusters (Table 1.3). Cotton and Dori (94,96) have prepared and characterized many easily attainable trinuclear metal cluster compounds. However, Müller *et al.* (84,86), Keck *et al.* (98), Shibahara *et al.* (99,100), Snow *et al.* (101) and Stiefel (102) have all reported many well characterized trinuclear, triangular metal cluster compounds. However, since these complexes were studied more recently than the majority of the hexanuclear species, their characterization (EXAFS, ^{95}Mo -NMR, single crystal structural analysis, etc.) (103-107) would be more refined. Surprisingly little literature has appeared recently on the hexanuclear systems.

Table 1.3. Compounds Containing Trinuclear Triangular
Ta, Nb, Cr, Mo, W Clusters.

No.	Compound	Average M-M A	Class	Oxid. State	Reactants, Method	Reference
1.	$[(Me_6C_6)_3Ta_3Cl_6]Cl$	N/A	A	7/3	N/A	108
2.	$[(Me_6C_6)_3Nb_3Cl_6]Cl$	2.334	A	7/3	N/A	108
3.	$[(Me_6C_6)_3Nb_3Br_6]Br$	N/A	A	7/3	$NbBr_5 + AlBr_3 + Al + C_6Me_6 \xrightarrow[sealed\ tube\ reaction]{dry\ N_2\ 130^\circ C/20\ hr}$	87, 88
4.	$[K_4(H_2O)_2][Nb_3O_2(SO_4)_6(H_2O)_3] \cdot 5H_2O$	2.885	C	11/3	$Nb + 70\% H_2SO_4 \xrightarrow[reduction]{electrolytic}$	90, 109
5.	$[Nb_3O_2(O_2CPh)_6(THF)_3][NbOCl_4(THF)]$	N/A	C	11/3	$Nb_2Cl_6(SMe_2)_3 + NaO_2CPh \xrightarrow{rt}$	91
6.	$[Nb_3O_2(O_2C-t-Bu)_6(THF)_3][BPh_4]$	2.842	C	11/3	Similar to 5 with the replacement of Ph by t-Bu	91
7.	Nb_3X_8 (X = Cl, Br, I)	N/A	C	8/3	$NbX_3 + Nb \xrightarrow[>500^\circ C]{stoichiometric}$	92
8.	$[S(Cr(CO)_4)_3]^{2-}$	N/A	B	0	$Cr(CO)_5THF + [Na][PPN]([Cr(CO)_5]_2) \xrightarrow{rt}$	83
9.	$[S(Cr(CO)_5)_3]^{2-}$	N/A	B	0	Ditto	
10.	$[Mo_3S_4(\eta-Cp)_3][Sn(CH_3)_3Cl_2]$	2.811	B	4	$Mo(\eta-Cp)(CO)_3Cl + [Sn(CH_3)_3]_2S \xrightarrow{DME}$	110
11.	$Mo_3S_7Cl_4$	2.745	B	6	$MoCl_3 + S_8 \xrightarrow[450/435^\circ C, 6\ days]{S_2Cl_2\ in\ a\ sealed\ tube,}$	111
12.	$[Mo_3S_{13}]^{2-}$	2.722	B	6	$(NH_4)_2S_x + (NH_4)_6Mo_7O_{24} \cdot 4H_2O + NH_4OH \cdot HCl \xrightarrow{rt}$	112
13.	$[Mo_3S_4(CN)_9]^{5-}$	2.766	B	4	$[Mo_3S_{13}]^{2-} + CN^- \xrightarrow{excess\ rt}$	86, 97, 101
14.	$[Mo_3S_7(R_2PS_2)_3]^+(R_2PS_2)^-$	2.737	B	6	$Mo(CO)_6 + (R_2PS)_2S_2 \xrightarrow{reflux}$	98
15.	$Mo_3S_6(R_2PS_2)_4$	N/A	B	4	$[Mo_3S_7(R_2PS_2)_3]^+(R_2PS_2)^- \xrightarrow{+R_3P; -R_3PS}$	115
16.	$[Mo_3S_4(SCH_2CH_2S)_3]^{2-}$	N/A	C	3	$(NH_4)_2Mo_3S_{13} + N(Et)_4Br + Na_2[SCH_2CH_2S] \xrightarrow{rt}$	122
17.	$Ca_3Mo_3S_4(Hnta)_2(nta) \cdot 26H_2O$	2.741	B	4	$[Mo_3S_4(H_2O)_9]^{4+} + H_3nta \xrightarrow{Ca\ salt}$	99
18.	$[Mo_3S_4(H_2O)_9]^{4+}$	N/A	B	4	$Mo(CO)_6 + Na_2S + \text{acetic anhydride} \xrightarrow[exchange]{ion}$	99, 126
19.	$[(Me_4N)_3]Mo_3S_4(NCS)_9$	N/A	B	4	$Na_2[Mo_2O_2S_2(cyst)_2] \cdot 3H_2O \xrightarrow[reduction]{electrolytic}$	127
20.	$Ba[Mo_3O_3S(Hnta)_3] \cdot 10H_2O$	2.589	B	4	$Mg[Mo_2O_3S(edta)] \cdot 6H_2O \xrightarrow[acid\ medium]{reduction\ in}$	100

Table 1.3. Cont'd

No.	Compound	Average M-M A	Class	Oxid. State	Reactants, Method	Reference
21.	$[\text{Cp}_2\text{Mo}_2(\text{CO})_6\text{S}]^+[\text{CpMo}(\text{CO})_3]^-$	3.085	B	2	$\text{Cp}_2\text{Mo}_2(\text{CO})_6 + \text{S}_8 \xrightarrow{\text{acetone}}$	114
22.	$[\text{Mo}_3\text{O}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_3]^{2+}$	2.486	B	4	$\text{Mo}^{\text{IV}} + \text{C}_2\text{O}_4^{2-} \xrightarrow[\text{aqueous soln}]{\text{rt}}$	103
23.	$[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$	N/A	B	4	$2/3 \text{ Na}_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O} \xrightarrow[\text{reductor}]{\text{Jones}}$ Mo(III) Then the remaining 1/3 added $\xrightarrow[90^\circ\text{C}]{\text{N}_2}$	105 105
24.	$\text{Mo}_3\text{O}_4(\text{OAc})_2(\text{NMe})_3]^{2+}$				Methyl iminodiacetic acid + Mo(IV) soln	105
25.	$\text{Mo}_3(\mu_3\text{-X})(\mu_3\text{-Y})(\text{OAc})_6$ $(\text{H}_2\text{O})_3(\text{anion})_x \cdot y\text{H}_2\text{O}$ X Y anion x y				$\text{Mo}(\text{CO})_6 + \text{HOAc} + (\text{Ac})_2\text{O}$ ion exchange ↓	117, 118
	O O Br 2 1	2.767	C	4		
	O O CF_3SO_3^- 2 0	2.757	C	4		
	O CCH_3 BF_4^- 1 9	2.753	C	10/3		
	CCH_3 CCH_3 SbF_6^- 1 3	2.815	C	3		
	CCH_3 CCH_3 CF_3SO_3^- 2 0	2.883	C	10/3		
	CCH_3 CCH_3 $\text{C}_7\text{H}_7\text{SO}_3^-$ 2 10	2.892	C	10/3		
26.	$[\text{Mo}_3\text{O}_2(\text{O}_2\text{CR})_6(\text{H}_2\text{O})_3]^{2+}$ R = Me	2.766	C	4	$\text{Mo}_2(\text{OAc})_4 + \text{RCOOH} + \text{RCO}_2\text{O}$ reflux 12 hrs ion exchange →	119
	R = Et	2.751	C	4		
27.	$([\text{Mo}_3\text{O}_2(\text{O}_2\text{CET})_6(\text{H}_2\text{O})_2]_2$ $(\text{H}_3\text{O}_2)_2\text{Br}_3 \cdot 6\text{H}_2\text{O}$	2.751	C	4	$\text{Mo}(\text{CO})_6 + \text{C}_2\text{H}_5\text{COOH} + (\text{C}_2\text{H}_5\text{CO})_2\text{O}$ reflux overnight ion exchange →	120
28.	$)\text{I}_3 \cdot 6\text{H}_2\text{O}$	2.751	C	4	Ditto	120
29.	$\text{Mo}_3\text{O}_2(\text{OAc})_6(\text{H}_2\text{O})(\text{OH})_2 \cdot 16\text{H}_2\text{O}$	2.785	C	4	$\text{Na}[\text{Mo}_3\text{O}_2(\text{OAc})_9] \xrightarrow{\text{acid}}$	94
30.	$\text{Na}[\text{Mo}_3\text{O}_2(\text{OAc})_9]$	N/A	C	4	$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} + \text{W}(\text{CO})_6 + (\text{Ac})_2\text{O}$ reflux 4 hrs/ N_2	94
31.	$\text{Mo}_3(\text{OAc})_6(\text{EtO})_2(\text{H}_2\text{O})_3]^{2+}$	2.854	C	10/3	$\text{Mo}(\text{CO})_6 + \text{AcOH} \xrightarrow[\text{exchange}]{\text{ion}}$	113
32.	$[(\text{Mo}_3\text{O}_4)_2(\text{EDTA})_3]^{4-}$	2.496	B	4	$\text{Mo}^{\text{IV}} \text{ soln} + \text{EDTA} \xrightarrow{\text{rt}}$	104
33.	$[\text{Zn}_2(\text{OAc})_3]^+[\text{Mo}_3\text{O}_2(\text{OAc})_6$ $(\text{OCH}_3)_3] \cdot 2\text{H}_2\text{O}$	2.782	B	4	$\text{Na}_2\text{MoO}_4 + \text{Zn}(\text{dust}) + (\text{Ac})_2\text{O} \xrightarrow[4 \text{ hr}]{\text{reflux}}$	165
34.	$(\text{NH}_4)_5[\text{Mo}_3\text{O}_4\text{F}_9] \cdot \text{NH}_4\text{F} \cdot \text{H}_2\text{O}$	2.505	B	4	$\text{Mo}^{\text{IV}} \text{ soln} + \text{HF soln.} + \text{NH}_4\text{F} \xrightarrow{\text{rt}}$	121
35.	$[\text{Mo}_3\text{O}_2(\text{O}_2\text{CPh})_6(\text{H}_2\text{O})_3]$ $(\text{ClO}_4)_2 \cdot \text{HClO}_4 \cdot 3\text{EtOH}$	2.763	C	4	$(\text{Ph-O})_2 + \text{Mo}_2(\text{OAc})_4 \xrightarrow[\text{exchange}]{\text{ion}}$	123
36.	$[\text{Mo}_3\text{OCl}_3(\text{OAc})_3(\text{H}_2\text{O})_3]$ $\text{ClO}_4 \cdot \text{Cl}$	N/A	C	10/3	$\text{Mo}(\text{CO})_6\text{Cl}_2 + \text{AcOH} + (\text{Ac})_2\text{O} \xrightarrow[\text{exchange}]{\text{ion}}$	166

Table 1.3. Cont'd

No.	Compound	Average M-M A	Class	Oxid. State	Reactants, Method	Reference
37.	$[W_3O_4F_9]^{5-}$	2.515	B	4	$(NH_4)_2[W_2O_4(C_2O_4)_2(H_2O)_2] \cdot 0.5$ $(NH_4)_2(C_2O_4) H_2O \xrightarrow{HF}$	124
38.	$W_3O_3Cl_5(OAc)(n-Bu_3P_3)$	N/A	C	4	N/A	in press
39.	$W_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ R = Me R = Et	2.746	C	4	$W(CO)_6 + RCOOH + (RCO)_2O \xrightarrow[\text{overnight}]{\text{reflux}}$	95
40.	$([W_3O_2(O_2C-t-Bu)_6](H_2O)(O_2C-t-Bu)_2)t-BuCOOH$	2.756	C	4	$W(CO)_6 + \text{Pivalic acid} \xrightarrow[48 \text{ hr}]{140^\circ C}$ sealed tube	95
41.	$([W_3O_2(OAc)_6](OAc)_3)^+$	2.771	C	4	$W(CO)_6 + (Ac)_2O + Et_3N \xrightarrow[24 \text{ hr}]{\text{reflux}}$	95
42.	$[Mo_3O_2(O_2CPh)_6(H_2O)_3]^{2+}$	N/A	C	4	$W(CO)_6 + PhCOOH \xrightarrow[36 \text{ hr}]{160^\circ C}$	123
43.	$([W_3O_2(O_2CET)_6(H_2O)_2](H_3O_2))Br_3 \cdot 6H_2O$	2.743	C	4	$W(CO)_6 + EtCOOH + (EtCO)_2O \longrightarrow$	120
44.	$]I_3 \cdot 6H_2O$	N/A	C	4	Ditto	120
45.	$]NCS$	N/A	C	4	Ditto + KSCN	120
46.	$[W_3O_2(O_2CET)_6(H_2O)_3]Cl_2 \cdot H_2O$	2.750	C	4	Same method as in 45	120
47.	$[W_3O(OAc)(H_2O)_3][ZnBr_4] \cdot 8H_2O$	2.708	B	8/3	$W(CO)_6 + ACOOH + ZnBr_2$	125
48.	$W_3(NH)(O-Pr)_{10}$	2.556	B	4	$W_2(O-Pr)_6(Py)_2 + (t-BuO)_3W \equiv N$ $\xrightarrow[1-PrOH]{22^\circ C/\text{hexane}}$	167

Ph = C_6H_5 , THF = C_4H_8O , t-Bu = $-C(CH_3)_3$, Me = CH_3 , Et = C_2H_5 , Pr = C_3H_7 , OAc = acetate, DME = 1,2-dimethoxyethane, H₃nta = nitrilotriacetic acid, rt = room temperature.

1.4.2 Compounds Containing Tetranuclear Metal Clusters

One of the important structural units of polynuclear metal cluster complexes is M_4X_4 cluster, where X is a non-metal atom. They are either cubane-like (tetrahedral) or rectangular (square planar). Because of the metal-to-metal bonding in these complexes, the cubane framework is more properly considered to be a tetrahedron of four metals with non-metal atoms capping the triangular faces (82a).

There are a few tetranuclear metal cluster compounds of Group VB and VIB elements where the non-metal atoms are O, F, Cl, NMe_2 and S (Tables 1.4 and 1.5). However, this class of compounds is dominated by complexes containing the Mo_4S_4 cluster core (Table 1.5). Both tables show that, with the exception of ligand replacement reactions, there is no general and systematic method to synthesize them. However, some of the complexes containing Mo_4S_4 clusters were prepared by the redox reactions of either dimeric sulfur-rich compounds and/or by the addition of excess sulfide ions to certain dimers. In addition, the formal oxidation states of molybdenum in these cluster compounds ranges from +3 to +3.5 (low oxidation states). Therefore, it is plausible to prepare these complexes by the reduction of dimeric sulfur-rich (if not, the presence of excess of sulfide ions is essential) compounds. In fact, there is evidence that the dimeric $Mo_2(S_2)_2(Et_2dtc)_4$, a compound prepared by the induced internal reduction of ammonium tetrathiomolybdate with tetraethylthiuram disulfide (144), can be reduced by hexacarbonyl-molybdenum to give a complex containing a Mo_4S_4 cluster core (144).

Table 1.4. Compounds Containing Mo_4X_4 Clusters, where $\text{X} \neq \text{S}$.

No.	Compound	Average M-M A	Oxid. State	Reactants, Method	Reference
1.	$\text{Mo}_4\text{F}_4(\text{O-Bu})_8$	2.263	3	$\text{Mo}_2(\text{O-t-Bu})_6 + \text{PF}_3 \longrightarrow$	128
2.	$\text{Mo}_4\text{F}_3(\text{NMe}_2)(\text{O-t-Bu})_8$	2.259	4	Ditto	130, 128
3.	$\text{Mo}_4\text{O}_8(\text{Me}_2\text{POS})_4$	2.635	5	$\text{MoCl}_5 + \text{Na}(\text{Me}_2\text{POS}) \xrightarrow{\text{reflux}}$	129
4.	$\text{Mo}_4\text{Cl}_8(\text{PR}_3)_4$	N/A	2	$\text{Mo}_4\text{Cl}_8(\text{EtCN})_4 + \text{PR}_3 \xrightarrow[6 \text{ hr}]{\text{rt}}$	131
5.	$\text{Mo}_4\text{Cl}_8(\text{CH}_3\text{OH})_4$	N/A	2	$\text{Mo}_2\text{Cl}_4[\text{PPh}_3]_2(\text{CH}_3\text{OH})_2 + \text{CH}_3\text{OH}/\text{HCl}$ $\xrightarrow[1 \text{ hr}/\text{N}_2]{\text{reflux}}$	131
6.	$\text{Mo}_4\text{Cl}_8(\text{EtCN})_4$	N/A	2	$\text{Mo}_4\text{Cl}_8(\text{CH}_3\text{OH}) + \text{EtCN} \xrightarrow{\text{rt}}$	131
7.	$\text{Mo}_4\text{Cl}_8(\text{THF})_4$	N/A	2	$\text{Mo}_4\text{Cl}_8(\text{EtCN}) + \text{THF} \xrightarrow[4 \text{ days}]{\text{reflux}}$	131
8.	$\text{Mo}_4\text{Cl}_8[\text{P}(\text{C}_4\text{H}_9)_3]_4$	N/A	2	$\text{K}_4\text{Mo}_2\text{Cl}_8 + \text{P}(\text{n-C}_4\text{H}_9)_3 \xrightarrow[1 \text{ day}]{\text{reflux}}$	131
9.	$\text{Mo}_4\text{Br}_8[\text{P}(\text{n-C}_4\text{H}_9)_3]_4$	N/A	2	$(\text{NH}_4)_4\text{Mo}_2\text{Br}_8 + \text{P}(\text{n-C}_4\text{H}_9)_3 \xrightarrow{0^\circ\text{C}}$ and $\text{Mo}_2(\text{OAc})_4 + \text{P}(\text{n-C}_4\text{H}_9)_3 +$ $(\text{CH}_3)_3\text{SiBr} \xrightarrow[1 \text{ day}]{\text{rt}}$	131 131
10.	$\text{Mo}_4\text{I}_8[\text{P}(\text{n-C}_4\text{H}_9)]_4$	N/A	2	$\text{Mo}_2(\text{OAc})_4 + \text{P}(\text{n-C}_4\text{H}_9)_3 + (\text{CH}_3)_3\text{SiI}$ $\xrightarrow[1 \text{ day}]{0^\circ\text{C}}$	131
11.	$[\text{Mo}_4\text{Cl}_4(\text{PR}_3)_2]_2$	N/A	2	$\text{Mo}_4\text{Cl}_4(\text{PR}_3)_4 + \text{Mo}(\text{CO})_4\text{Cl}_2 \xrightarrow{\text{heat}}$	131a
12.	$\text{W}_4\text{Cl}_8\text{L}_4$	N/A	2	N/A	131b

Table 1.5. Compounds Containing M_4S_4 Clusters, where $M = Cr, Mo$.

No.	Compound	Average M-M Δ	Oxid. State	Reactants, Method	Reference
1.	$Cr_4S_4(Cp)_4$	N/A	3	N/A	132
2.	$Mo_4S_4(Cp)_4$	N/A	3	N/A	133
3.	$Mo_4S_4(Ntol)_4[(EtO)_2PS_2]_4$	2.862	3	$Mo(Ntol)[(EtO)_2PS_2]_3 \xrightarrow{\text{reflux}}$	134, 143
4.	$K_8[Mo_4S_4(CN)_{12}] \cdot 4H_2O$	2.855	3	$MoS_3 + KCN \xrightarrow{rt}$ $(NH_4)_2MoS_4 + KCN \xrightarrow{rt}$	137 97
5.	$(NH_4)_2[Mo_4(NO)_4(S_2)_6O] \cdot 2H_2O$ $NH_4K[Mo_4(NO)_4(S_2)_6O] \cdot 2H_2O$	{ 3.309 3.942 }	3	$MoO_4^{2-} + NH_4OH \cdot HCl \xrightarrow{H_2S}$	135
6.	$[Mo_4S_4(NO)_4(CN)_8] \cdot 4H_2O$	2.990	3	$[Mo_4(NO)_4(S_2)_6O]^{2-} \xrightarrow{KCN}$	136
7.	$Mo_4S_4(Et_2PS_2)_6$	N/A	14/4	N/A	138
8.	$Mo_4S_4(C_5H_4-Pr)_4^{n+}$ $n = 0$ $= 1$ $= 2$	2.858 2.894 2.904	3 13/4 14/4	$[Mo(C_5H_4-Pr)Cl_2]_2 \xrightarrow{LiHS}$ $Mo_4S_4(C_5H_4-Pr) \xrightarrow{dil/HCl}$ $Mo_4S_4(C_5H_4-Pr) \xrightarrow{I_2/toluene}$	139
9.	$Mo_4S_4(Ntol)(Bu_2dtc)_4$	2.881	3	$Mo_4S_4(Ntol)_4[(EtO)_2PS_2] + S_2CNBu_2^- \xrightarrow{\text{reflux}}$	140
10.	$Ca_3[Mo_4S_4(edta)_2]_2$	2.808	13/4	$Na_2[Mo_2O_2S_2(edtc)_2] \cdot 2H_2O + NaBH_4 \xrightarrow{dil/HCl}$	141
11.	$Mo_4S_4(Et_2dtc)_6$	2.800	14/4	$Mo_2(Et_2dtc)_6 \xrightarrow{\text{reflux toluene}}$	142
12.	$Na_3[Mo_4S_4(edta)_2]$	N/A	13/4	electrochemical reduction of $Na_2[Mo_2O_2S_2(cyst)_2] \cdot 3H_2O$ in 2M HCl	127
13.	$(NH_4)_6[Mo_4S_4(NCS)_{12}]$	N/A	14/4	$Mo(CO)_6 + Na_2S + (Ac)_2O \xrightarrow{\text{ion exchange}}$	126

1.4.3 Compounds Containing Hexanuclear Metal Clusters

Compounds with the clusters $[M_6X_8]$ and $[M_6X_{12}]$, where X = halogen, are known for the early heavy transition metals (145). When M = Mo or W the first type is generally formed, and when M = Nb or Ta the second. The exception to this rule are $[Nb_6I_8]I_{6/2}$ (146), $[W_6Cl_{12}]Cl_6$ (147) and $[Mo_6Cl_{12}]Cl_6$ (159,160). For extensive reviews see references 156 and 157.

The most common geometry observed in the cluster chemistry of Nb and Ta is the octahedron formed by the six mutually bonded metal atoms. This can be exemplified by the above-mentioned general formulae. The twelve μ_2 -bridging halogen atoms are located over the twelve octahedral edges (148). Each metal atom has one site open to accept a terminal ligand. This indicates that a larger unit having the formula $[(M_6X_{12})L_6]^{4-}$ with $[M_6X_{12}]^{2+}$ cluster may be prepared, where L are ligands terminally bonded to the metals through the six open sites. However, these coordinatively unsaturated sites can also bind to neutral electron donating ligands containing oxygen, nitrogen and phosphorus donors (149). The complexes M_6X_{14} are usually the starting materials to prepare the above series of compounds (149). There are three principle methods of preparation which include: (a) reduction of the appropriate metal pentahalide with Cd or Al at red heat; (b) disproportionation of Nb_3X_8 in the presence of an alkali halide in niobium tubes or in the presence of niobium metal; (c) conproportionation of the metal with its pentahalide in the presence of an alkali halide. The last reaction appears to be the method of choice in which the halide clusters are isolated by aqueous extraction and HX treatment (150).

In all of these complexes the $[M_6X_{12}]^{2+}$ cluster core react as a unit. They can undergo one or two electron transfer reactions with only slight

structural distortion. Most of their reactions involve the substitution of the terminally bound halogen ligands (149).

The complex $[\text{Nb}_6\text{I}_8]\text{I}_3$ (146) contains an example of an octahedral niobium or tantalum cluster which is face-capped with eight μ_2 -bonded iodine atoms rather than twelve edge-bridged by μ_2 -halide which is the most common feature in complexes containing the $[\text{M}_6\text{X}_{12}]$ cluster. The remaining six iodine atoms extend radially outward from the six apices of the Nb_6 octahedral cluster. This cluster compound can be reduced by hydrogen gas near 400°C to form $\text{Nb}_6\text{I}_{11}\text{H}$, the hydrogen atom being located within the cluster (151). It reacts with niobium and caesium iodide in a sealed niobium tube at 910°C to give $\text{CsNb}_6\text{I}_{11}$ (152) from which the cluster compound $\text{CsNb}_6\text{I}_{11}\text{H}$ can be prepared by reaction with H_2 at 400°C (152).

Recently, very interesting sulfur-rich complexes of Ta and Nb have been reported. Complexes containing the anion $[\text{M}_6\text{S}_{17}]^{4-}$ ($\text{M} = \text{Ta}, \text{Nb}$) are easily attainable by the reaction of $\text{M}(\text{OEt})_5$, $(\text{Me}_3\text{Si})_2\text{S}$ and Et_4NCl (all of them are commercially available) in acetonitrile (153). Although these complexes do not contain any cluster core as each two adjacent Mo atoms are doubly bridged by two sulfur atoms without metal-to-metal bonds, its rare five-fold C_{5v} symmetric structure is worth investigating.

The most common geometry of the metals in the cluster unit $[\text{M}_6\text{X}_8]^{4+}$ ($\text{M} = \text{Mo}, \text{W}$ and $\text{X} = \text{halogen}$) is the M_6 octahedron where the formal oxidation state of the metal is usually +2. The eight μ_3 -halogen ligands symmetrically cap the eight faces of the metal skeleton, so that this structure is identical to that of the $[\text{M}_6\text{I}_8]^{3+}$ unit in $[\text{M}_6\text{I}_8]\text{I}_3$ compounds ($\text{M} = \text{Ta}, \text{Nb}$) (146). The six metal atoms in this unit are frequently coordinated to six terminal ligands, extending radially outward from the apices of the octahedron (146).

Generally, complexes containing this cluster unit are prepared by thermal decomposition of their higher halides or direct halogenation of the metals at temperatures sufficiently high to decompose the higher halides (154-159).

In the presence of excess halogen, compounds containing $[M_6X_8]^{4+}$ clusters ($M = Mo, W$) may be oxidized to others containing the $[M_6X_{12}]^{6+}$ unit (147,159). These compounds are isostructural with their Ta and Nb counterparts. It might be expected that the non-cluster halogens should be readily replaced by other halogens. Indeed for $[M_6X_8]Y_4$, mixed halides of all possible combinations of X and Y (Cl, Br, I) are known (160,161). In addition, these compounds function as Lewis acids (156). Bonding of each metal atom to one donor organic molecule results in retaining the basic structural unit. Coordination of two unidentate ligands to the $[M_6X_8]^{4+}$ cluster destroys the intercluster bonding, but the coordination of a third or fourth ligand occurs only with the ionization of the halogen. However, coordination of bidentate ligands to the cluster $[M_6X_8]^{4+}$ leads to significant distortion of the octahedron (162). It has been found that in Mo_6Cl_{12} and Mo_6Br_{12} , replacement of the halogen by alkoxide is feasible at room temperature to give $Na_2[(Mo_6X_8)(OR)_6]$ ($X = Cl, Br$) in which the $[M_6X_8]^{4+}$ unit remains intact (163). Tables 1.6-1.11 shows a variety of M_6 cluster compounds and their preparations.

1.5 Selection of the Metal Cluster Compounds

It is apparent that the compounds of choice should be selected from complexes containing the following cluster cores: Nb_3 , Mo_3 , W_3 , Mo_4 , Nb_6 , Ta_6 , Mo_6 and W_6 because compounds containing Ta_3 and W_4 are not abundant.

Table 1.6. Preparation of Niobium and Tantalum Halides $M_6X_{12}X_6$, and Halogeno Complex Ions $[(M_6X_{12})X_6]^{2-}$.*

No.	Compound	Reactants	Method
1.	$Ta_6Cl_{16} \cdot 7H_2O$	$Ta_6Cl_{14} \cdot 9H_2O$, H_2O_2	Oxid
2.	$Ta_6Br_{16} \cdot 7H_2O$	$Ta_6Br_{14} \cdot 8H_2O$, excess $KBrO_3$	Oxid
3.	$Nb_6Cl_{16} \cdot 3C_2H_5OH$	$Nb_6Cl_{14} \cdot 8H_2O$	Aerial oxidn, 2 months
4.	$[Nb_6Cl_{12}]^{4+}$ (soln)	$[Nb_6Cl_{12}]^{2+}$	Oxidn by $Fe(III)$, I_2
5.	$[Nb_6Br_{12}]^{4+}$ (soln)	$[Nb_6Cl_{12}]^{2+}$	Oxidn in acid soln
6.	$[Ta_6Cl_{12}]^{4+}$ (soln)	$[Ta_6Cl_{12}]^{2+}$	Oxidn by $Fe(III)$, Cl_2
7.	$[Ta_6Br_{12}]^{4+}$ (soln)	$[Ta_6Br_{12}]^{2+}$	Oxidn by $Fe(III)$, Br_2 , BrO_3^- , or $V(V)$
8.	$[(Nb_6Cl_{12})Cl_6]^{2-}$	$Nb_6Cl_{14} \cdot 8H_2O$	Oxidn with Cl_2 or H_2O_2 , isolate as Et_4N^+ , pyH^+ salts
9.	$[(Nb_6Br_{12})Cl_6]^{2-}$	$(Nb_6Br_{12})Cl_2 \cdot 8H_2O$	Oxidn with H_2O_2 , pyH^+ salt in acid soln
10.	$[(Ta_6Cl_{12})Cl_6]^{2-}$	$[Ta_6Cl_{12}]^{2+}$	Oxidn in air or H_2O_2 , acid soln, pyH^+ , Ph_4As^+ salts
11.	$[(Ta_6Cl_{12})Br_6]^{2-}$	$[Ta_6Cl_{12}]^{2+}$	Aerial oxidn in HBr , Et_4N^+ salt

* References 149, 150, 156, 157.

Table 1.7. Preparation of Niobium and Tantalum Halides M_6X_{15} and Halogeno Complexes $[(M_6X_{12})X_6]^{3-}$ and $Nb_4X_{11}^-$.*

No.	Compound	Reactants	Method
1.	Nb_6F_{15}	NbF_5 , Nb; or NbF_4	Temp gradient 400/300°C; or > 700°C
2.	$Nb_6Cl_{15} \cdot 7H_2O$	$Nb_6Cl_{14} \cdot 8H_2O$, H_2O_2	Oxidn in acid (HCl) soln
3.	$Ta_6Cl_{15} \cdot 7H_2O$	$Ta_6Cl_{14} \cdot 8H_2O$, air	Oxidn in air, 1 week; also hexahydrate has been obtained
4.	$Ta_6Cl_{12}Br_3 \cdot nH_2O$	$Ta_6Cl_{14} \cdot 8H_2O$	Aerial oxidn of HBr soln
5.	$Ta_6Br_{15} \cdot nH_2O$ (n = 6, 8)	$Ta_6Br_{14} \cdot 8H_2O$, air or $KBrO_3$	Oxidn in air or with $KBrO_3$ in acid soln
6.	Ta_6Cl_{15}	$TaCl_5$, Al $TaCl_5$, Ta	Temp gradient 400/200°C, then 550°C for residue Temp gradient 630/315°C or 625/298°C
7.	Ta_6Br_{15}	$TaBr_5$, Ta $TaBr_{2.83}$, Ta $TaBr_5$, Al	Temp gradient 603/330°C or 635/350°C 606°C As per Ref. 168
8.	$[Ta_6I_{12}]I_{18}$	Ta_6I_{14} , I_2	Heat 250°C (polyiodide)
9.	$[Ta_6I_{15}]$	$[Ta_6I_{12}]I_{18}$	Heat, vacuo, 100–200°C
10.	$[Ta_6Cl_{12}]^{3+}$ (soln)	$[Ta_6Cl_{12}]^{2+}$ $[Ta_6Cl_{12}]^{2+}$, $[Ta_6Cl_{12}]^{4+}$	Oxidn by Fe(III), Hg(II), Ce(IV), Cu(II), cis- $[Co(NH_3)_4(OH_2)Cl]^{2+}$ Redox reaction
11.	$[Ta_6Br_{12}]^{3+}$ (soln)	$[Ta_6Br_{12}]^{2+}$	Oxidn by V(v), BrO_3^-
12.	$[Nb_6Br_{12}]^{3+}$ (soln)	$[Nb_6Br_{12}]^{2+}$	Oxidn in acid soln
13.	$[(Nb_6Cl_{12})Cl_6]^{3+}$, (Et_4N^+)	$Nb_6Cl_{14} \cdot 8H_2O$	Aerial oxidn or by I_2 in EtOH/HCl soln
14.	$[(Nb_6Cl_{15})Cl_5OH]^{3-}$, (Ph_4As^+)	$Nb_6Cl_{14} \cdot 8H_2O$	Aerial oxidn in HCl soln vary acidity for required product
15.	$[(Nb_6Cl_{12})Cl_4OH]^{2-} \cdot H_2O$, (Ph_4As^+)	Ditto	Ditto
16.	$[(Nb_6Cl_{12})Cl_5]^{2-} \cdot H_2O$, (Ph_4As^+)	Ditto	Ditto
17.	$[(Ta_6Cl_{12})Cl_6]^{3-}$, (Et_4N^+)	$Ta_6Cl_{14} \cdot 7H_2O$	Oxidn
18.	$Nb_4Cl_{11}^-$, $(Cs^+$, $Rb^+)$	Nb_3Cl_8 , Nb, MCl	Temp gradient 730/700°C
19.	$Nb_4Br_{11}^-$, (Cs^+)	Nb_3Br_6 , Nb, CsBr	Temp gradient 630/610°C; ext by HBr soln

* References 149, 150, 156, 157.

Table 1.8. Preparation of Niobium and Tantalum Halides M_6X_{14} , Complexes $M_6X_{14}L_4$, and Halogeno Complexes $[(M_6X_{12})X_6]^{4-}$.

No.	Compound	Reactants	Method
1.	$Nb_6Cl_{14} \cdot 7H_2O$ or $8H_2O$ and $9H_2O$	$NbCl_5$, Na/Hg $NbCl_5$, Zn or Al or Mg or Cd	High temp; ext into H_2O High temp; Cd best metal to use (116)
2.	$(Nb_6Cl_{12})(OH)_2 \cdot 8H_2O$	$Nb_6Cl_{14} \cdot 8H_2O$ in alkali	
3.	$(Nb_6Cl_{12})Br_2 \cdot 7H_2O$ or $8H_2O$	$Nb_6Cl_{14} \cdot 8H_2O$	In hydroxide treated with HBr
4.	$(Nb_6Cl_{12})I_2 \cdot nH_2O$	$Nb_6Cl_{14} \cdot 8H_2O$	In hydroxide treated with HI
5.	$M_6X_{12}(BF_4)_2 \cdot nH_2O$ (M = Nb, Ta; X = Cl, Br)	$Nb_6Cl_{14} \cdot 8H_2O$	Add BF_4^- to satd soln
6.	$M_6X_{12}(SO_4)_2 \cdot nH_2O$ (M = Nb, Ta; X = Cl, Br)	$Nb_6Cl_{14} \cdot 8H_2O$	Add SO_4^{2-} to satd soln
7.	$(Nb_6Cl_{12})(ClO_4)_2 \cdot (DMSO)_8$	$Nb_6Cl_{14} \cdot 8H_2O$	Add $AgClO_4$, then DMSO
8.	$(Nb_6Cl_{12})Cl_2L_4$	$Nb_6Cl_{14} \cdot 8H_2O$ + ligand	L = DMSO, DMF, Ph_3PO , PR_3 , Ph_3AsO , $pyNO$, $R-C_5H_4NO$
9.	$Nb_6Br_{14} \cdot 7H_2O$ or $8H_2O$	$NbBr_5$, Cd $NbBr_5$, Al	High temp; ext into HBr soln Thermal gradient
10.	$Ta_6Cl_{14} \cdot 7H_2O$ or $8H_2O$	$TaCl_5$, Na/Hg $TaCl_5$, Pb $TaCl_5$, Cd	Red heat; ext into H_2O At $600^\circ C$ Red heat; ext into acidified water
11.	$(Ta_6Cl_{12})Br_2 \cdot 7H_2O$	$Ta_6Cl_{14} \cdot 8H_2O$	Treat chloride with HBr
12.	$(Ta_6Cl_{12})Br_2 \cdot 2H_2O$		Heat heptahydrate
13.	$Ta_6Cl_{14}(py)_2$	$[(Ta_6Cl_{12})Cl_6]^{4-}$, pyH^+ salt	Heat to $290^\circ C$
14.	$Ta_6Cl_{14}L_4$	$Ta_6Cl_{14} \cdot 8H_2O$	Crystallize from L = py, EtOH, PR_3
15.	$Ta_6Br_{14} \cdot 7H_2O$ or $8H_2O$	$TaBr_5$, Na/Hg $TaBr_5$, Cd	Red heat, ext into aq HBr Red heat, ext into aq HBr
16.	$(Ta_6Br_{12})(OH)_2 \cdot 10H_2O$	$Ta_6Br_{14} \cdot 8H_2O$	Add alkali
17.	$(Ta_6Br_{12})X_2 \cdot 7H_2O$ (X = Cl, I)	Hydroxide	Add HX and crystallize
18.	$Nb_xTa_yBr_{14} \cdot 8H_2O$	$NbBr_5$, $TaBr_5$, Cd	Red heat and extn
19.	Nb_6Cl_{14}	Nb_3Cl_8	Thermal disprop

Table 1.8. Cont'd

No.	Compound	Reactants	Method
20.	$\text{Nb}_6\text{Br}_{14}$	NbBr_5 , Al	Thermal gradient
21.	Nb_6I_{14}	NbI_5	Heat, vacuo, 300-400°C
22.	$\text{Ta}_6\text{Br}_{14}$	TaBr_5 , Al	Temp gradient 450/280°C
23.	Ta_6I_{14}	TaI_5 , Ta	Temp gradient 630/575°C or 660/510°C or one temp 500°C
		TaI_5 , Al	Temp gradient 475/300°C
		$[\text{Ta}_6\text{I}_{12}]\text{I}_{18}$	Treat with Cd
24.	$[(\text{Nb}_6\text{Cl}_{12})\text{X}_4]^{2-}(\text{EtOH})_2$ (X = Cl, Br), Et_4N^+ salt	$\text{Nb}_6\text{Cl}_{14}8\text{H}_2\text{O}$	In EtOH add excess Et_4NX
25.	$[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{4-}$, Et_4N^+ salt K^+ salt	$\text{Nb}_6\text{Cl}_{14}8\text{H}_2\text{O}$	Add cation to EtOH/HCl soln
		Nb_3Cl_9 , KCl	In Mo or Nb tubes, 600-900°C
		Nb_3Cl_9 , Nb, KCl/LiCl	Heat to molten state
		$\text{Nb}_6\text{Cl}_{14}$, KCl	Heat 1:4 mixt to 650°C
26.	$[(\text{Nb}_6\text{Cl}_{12})\text{Br}_6]^{4-}$, Et_4N^+ salt	$\text{Nb}_6\text{Cl}_{14}8\text{H}_2\text{O}$	Add cation to EtOH/HBr soln
27.	$[(\text{Nb}_6\text{Cl}_{12})\text{I}_6]^{4-}$ CH_3pyH^+ salt	$\text{Nb}_6\text{Cl}_{14}8\text{H}_2\text{O}$	Add cation to halide and treat with HI gas
28.	$[(\text{Nb}_6\text{Br}_{12})\text{Br}_6]^{4-}$, Rb^+ salt	Nb_3Br_9 , RbBr	Heat 710°C, mixt of products formed, low yield
29.	$[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6]^{4-}$, K^+ salt pyH^+ salt	TaCl_5 , Al, KCl	Heat to 550°C
		$\text{Ta}_6\text{Cl}_{14}8\text{H}_2\text{O}$	Add py to EtOH/HCl soln of chloride

* References 149, 150, 156, 157.

Table 1.9. Preparation of Molybdenum and Tungsten Divalent Halides.*

No.	Compound	Reactants	Method and Comments
1.	$(\text{Mo}_6\text{Cl}_8)_2\text{Cl}_4$	MoCl_5 , Mo MoCl_3 MoCl_3 , Mo MoCl_5 , H_2 MoCl_3 , H_2 Mo, COCl_2 , $[(\text{Mo}_6\text{Cl}_8)_2\text{Cl}_4]^{2-}$ Ph_3PH^+ salt	Heat, get MoCl_3 ; heat to give MoCl_2 , cryst as acid, heat 200°C Heat 500-650°C, 340°C, or temp gradient 950/850°C Thermal grad 750/550°C 450-650°C; mixed product 350-410°C; mixed product 600°C; inefficient Heat 500°C
2.	βMoCl_2	Mo(II) acetate, HCl gas	-250°C, esp in O_2 free conditions
3.	$\text{Mo}_6\text{Br}_8\text{Br}_4$	MoCl_2 , LiBr MoBr_3 Mo, Br_2 Mo, HBr_{aq}	Fuse 450-500°C, ext into acid, cryst, and heat in vacuo 200°C Thermal disprop 500-650°C Temp around 600-700°C 700°C, ST, 3000 atm; get dihydrate
4.	$\text{Mo}_6\text{I}_8\text{I}_4$	MoCl_2 , LiI MoI_3 Mo, I_2 MoO_2 , AlI_3	Fuse 450-550°C, ext into HI soln, cryst, heat in vacuo 200°C Heat 100 or 500°C in vacuo 400-500°C 230°C, ST
5.	$\text{W}_6\text{Cl}_8\text{Cl}_4$	WCl_6 , P WCl_6 , H_2 WCl_4	Heat; P impurity Heat; product impure Heat 500°C, in vacuo, 300-600°C, temp gradient 450/500°C, 400/450°C
6.	$\text{W}_6\text{Br}_8\text{Br}_4$	WBr_5 , H_2 WBr_4 W, Br_2	<500°C Temp gradient 500/450°C, then 600°C Temp gradient 760/560°C
7.	$\text{W}_6\text{I}_8\text{I}_4$	WCl_6 , HI soln $\text{W}(\text{CO})_6$, I_2	110°C, then heat product 500°C in vacuo Temp gradient 450/300°C, then 500-600°C
8.	$[(\text{Mo}_6\text{Cl}_8)_2\text{Cl}_3\text{OH}]\cdot 2\text{H}_2\text{O}$	Chloro acid in water	Warm dry product 130°C
9.	$\text{Mo}_6\text{Cl}_8\text{Br}_4$	MoCl_2 , HBr	Heat cryst 200°C in vacuo
10.	$\text{Mo}_6\text{Cl}_8\text{I}_4$	MoCl_2 , HI	Heat cryst 200°C in vacuo
11.	$\text{Mo}_6\text{Cl}_6(\text{OH})_4\cdot 14\text{H}_2\text{O}$	MoCl_2 , $\text{NH}_3/\text{NH}_4\text{NO}_3$ buffer	Heat product 25°C in vacuo, get dihydrate
12.	$\text{Mo}_6\text{Cl}_8(\text{OH})_4$	Dihydrate	Heat in vacuo 200°C
13.	$\text{Mo}_6\text{Br}_8\text{Cl}_4$	MoBr_2 , HCl	Heat ppt to 220°C
14.	$\text{Mo}_6\text{Br}_8\text{I}_4$	MoBr_2 , HI	Heat ppt to 220°C
15.	$\text{Mo}_6\text{Br}_8(\text{NO}_3)_4$	MoBr_2 , AgNO_3	Reflux EtOH soln

Table 1.9. Cont'd

No.	Compound	Reactants	Method and Comments
16.	$\text{Mo}_6\text{Br}_8(\text{OH})_4$	MoBr_2 , alkali	Obtain $14\text{H}_2\text{O}$, heat in vacuo 25°C Obtain $2\text{H}_2\text{O}$, heat in vacuo 200°C
17.	$\text{Mo}_6\text{I}_8\text{Cl}_4$	MoI_2 , HCl	Heat cryst to 220°C in vacuo
18.	$\text{Mo}_6\text{I}_8\text{Br}_4$	MoI_2 , HBr	Heat cryst to 220°C in vacuo
19.	$[\text{Mo}_6\text{X}_8\text{-n}(\text{OH})\text{n}]^{4+}$ ($\text{X} = \text{Cl}, \text{I}$)	MoX_2 , alkali	

* References 147, 155, 158, 162.

Table 1.10. Preparation of Molybdenum and Tungsten Halogeno Complexes $[(M_6X_8)X'_6]^{2-}$.*

No.	Compound	Reactants	Method and Comments
1.	$[(Mo_6Cl_8)Cl_6]^{2-}$	$MoCl_2$, $HCl(aq)$, cation	Cryst of salt; Reactions also done in EtOH soln or by first preparing the tetrahydroxide; $(Ph_3AsO)_2H^+$, $(Ph_3PO)_2H^+$, Ph_3AsOH^+ , K^+ , Et_4N^+ , Cs^+ , Ph_4As^+ , Me_4N^+ , Bu_4N^+ , H_3O^+ , NH_4^+ , Ph_3PH^+ , bipy H^+ , py H^+)
2.	$[(Mo_6Cl_8)Br_6]^{2-}$	$MoCl_2$, HBr , cation	In EtOH soln also or remove terminal Cl's with Ag^+ (Bu_4N^+ , H_3O^+)
3.	$[(Mo_6Cl_8)I_6]^{2-}$	$MoCl_2$, HI , cation	In EtOH soln (Bu_4N^+ , H_3O^+ , bipy H^+)
4.	$[(Mo_6Cl_8)(NCS)_6]^{2-}$	$MoCl_2$, $KNCS$	$K^+(H_2O)$ salt, compound impure
5.	$[(Mo_6Cl_8)(OH)_6]^{2-}$	$MoCl_2$, alkali	In solution only
6.	$[(Mo_6Cl_8)(OR)_6]^{2-}$	$MoCl_2$, ROH , $NaOR$	Reflux, Na^+ salt, $R = Me, Et$; also can replace $R = Me$ with $R = Et, Ph$ (distn)
7.	$[(Mo_6Br_8)Cl_6]^{2-}$	$Mo_6Br_8Cl_4$, HCl , or alkali, then HCl	Add cation (pyH^+ , Et_4N^+)
8.	$[(Mo_6Br_8)Br_6]^{2-}$	As above or EtOH soln $MoBr_2$, MBR in IBr $MoBr_2$, IBr	(pyH^+ , Et_4N^+) salts At $50^\circ C$ (Cs^+ , Rb^+) I^+ salt
9.	$[(Mo_6Br_8)I_6]^{2-}$	$Mo_6Br_8I_4$, HI + cation in EtOH solution	Salts (pyH^+ , Et_4N^+ , Me_4N^+)
10.	$[(Mo_6Cl_7)(OH)Cl_6]^{2-}$	$MoCl_2$, alkali + cation/ HCl	Obtain Et_4N^+ salt
11.	$[(Mo_6Cl_4Br_3OH)Br_6]^{2-}$	As above	Obtain Et_4N^+ salt
12.	$[Mo_6Br_8(OCH_3)_6]^{2-}$	$MoBr_2$, $MeOH$, $NaOMe$	Reflux (Na^+ salt)
13.	$[(Mo_6I_8)Cl_6]^{2+}$	As for $[(Mo_6Br_8)I_6]^{2-}$ above	Obtain (pyH^+ , Et_4N^+)
14.	$[(Mo_6I_8)Br_6]^{2+}$	As above	Obtain (pyH^+) salt
15.	$[(Mo_6(OCH_3)_9(OCH_3)_6]^{2-}$	$MoCl_2$, $MeOH$, $NaOCH_3$	Heat $150^\circ C$ (Na^+)
16.	$[(Mo_6(OCH_3)_9(OPh)_6]^{2-}$	Compounds above, $PhOH$	At room temp (Na^+)
17.	$[(Mo_6(OCH_3)_4(OPh)_4(OPh)_6]^{2-}$	Compounds above	Heat to $100^\circ C$
18.	$[(W_6Cl_8)Cl_6]^{2-}$	WCl_2 , $EtOH$, HCl or WCl_2 , $NaOH$, HCl	Add cation Et_4N^+
19.	$[(W_6Cl_8)Br_6]^{2-}$	WCl_2 , HBr , cation	In EtOH

* References 147, 155, 158, 162.

Table 1.11. Preparation of Neutral Ligand Complexes of Molybdenum and Tungsten Dihalides.*

No.	Compound	Reactants	Method and Comments
1.	$[(Mo_6Cl_8)Cl_4L_2]$ (L = monodentate ligands)	$MoCl_2$, ligand, solvent if necessary	Ppt or cryst comp'ax, sometimes re-flux is necessary: L = H_2O , Et_3N , py, Ph_3PO , Ph_3AsO , DMF, DMSO, MeCN, EtCN, nPrCN, and picoline, quinoline, pyrazine, acetone, EtOH, THF, pyNO, Ph_3P , NH_3 , 1.4 thioxan, R- C_6H_4NO
2.	$(Mo_6Cl_8)Cl_4L_3$	As above	L = Ph_3P
3.	$(Mo_6Cl_8)Cl_4L_4$	As above	L = NH_3 , PMS
4.	$(Mo_6Cl_8)Cl_4L_2L'_2$	As above	LL' = Ph_3P , EtOH; Ph_3P , py; NNTu, EtOH
5.	$(Mo_6Cl_8)Br_4(H_2O)_2$	-	-
6.	$(Mo_6Cl_8)I_4L_2$	$(Mo_6Cl_8)I_4$, ligand	L = pyridine
7.	$(Mo_6Br_8)Br_4L_2$	$MoBr_2$, ligand	L = pyridine
8.	$(Mo_6I_8)X_4L_2$ (X = Cl, Br)	Halide, ligand	L = pyridine
9.	$Mo_6Cl_8(CH_3SO_3)_4L_2$	$MoCl_2$, $AgCH_3SO_3$, ligand	Remove AgCl, then add L = DMF, DMSO
10.	$Mo_6Cl_8Cl_4(LL)_2$	$MoCl_2$, ligand in solvent (acid soln has also been used)	Cryst or ppt, LL = o-phen, bipy, diars, TMED, DTH
11.	$Mo_6Cl_8Cl_4(LL)$ (LL is bidentate)	$MoCl_2$, ligand, solvent	LL = diphos in ST, 130°C; also get $Mo_6Cl_8Cl_4(diphos)py$
12.	$(Mo_6Cl_8)I_4(LL)_2$ (LL is bidentate)	$Mo_6Cl_8I_4$, solvent, ligand	LL = bipy, o-phen
13.	$Mo_6Cl_8X_4(terpy)$	$Mo_6Cl_8X_4$, solvent, terpyridyl	
14.	$[(Mo_6Cl_8)L_6]^{4+}$	$MoCl_2$, in MeOH, $AgClO_4$, ligand	Add $AgClO_4$ to $MoCl_2$, then remove AgCl and add L = DMSO, DMF

* References 147, 155, 158, 162.

Since no supported metal cluster catalysts of Nb, Ta, Mo or W have yet been prepared, it is rather difficult to predict the appropriate size (nuclearity) and environment (ligand) of the suitable cluster unit. However, because of the ease of preparation, relatively simple solution chemistry and recent accurate characterization, the oxo-, sulfido, or mixed oxo-sulfido-trinuclear metal cluster compounds of Nb, Mo and W may be considered an excellent choice for the catalyst preparation. Supporting these cluster compounds on inorganic supports should greatly enhance their stability. However, such catalysts need to be stable under conditions of high temperature and pressure, and stability may therefore be a problem. For example, reactions at high temperature and under reducing conditions may lead to the formation of clusters with a higher degree of nuclearity. Another possible choice is compounds containing the tetranuclear metal cluster Mo_4X_4 (where X = halogen, oxygen, or sulfur); and the metals are either tetrahedral (cubane-like) or planar (rectangular). These cluster compounds are relatively more stable than their trinuclear counterparts. The last possible selection may be compounds containing the hexanuclear metal framework in an octahedral geometry. Their high thermal stability is a desired major criterion for industrial catalysts.

The aqueous chemistry, redox behaviour and ligand exchange reactions in the above classes of cluster compounds may be utilized to immobilize them on hydroxylated inorganic solid supports (e.g. $\gamma\text{-Al}_2\text{O}_3$, $\text{F}^-/\gamma\text{-Al}_2\text{O}_3$, SiO_2) which may permit facile cluster-supporting reactions.

A reasonable and valid expectation of catalytic activity may be drawn by comparison with the well-known catalytic behaviour of monomeric Nb, Mo and W compounds as well as the pairs in the dimers $\text{Cr}_2(\eta^3\text{-C}_3\text{H}_5)_4$, $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$ and

Nb_2O_5 . The choice of redox reactions, particularly hydrotreating, is attractive for these catalysts because of the multiple reaction centres and the availability of the delocalized cluster-core electrons. They may also show some novel catalytic reactions due to the geometry of their metal frameworks. Some preliminary studies of the preparations and reactions of certain cluster compounds with support materials would give an indication of the probability of success.

A preliminary screening process of the vast number of cluster compounds of Groups VB and VIB available in the literature (see text) has been made. The selection is mainly based on the relative ease of preparation and handling of the complexes, availability of reliable characterization data and accessibility to chemicals and equipments. The candidate compounds after screening are:

Table No.	Compound No.
1.3	3-5, 12-18, 21, 22, 24, 29, 30, 32-34, 36, 37-47
1.4	1, 3-11
1.5	3-6, 8, 9
1.8	1, 9, 10, 15
1.9	1, 3-7
1.11	1-8, 10-13

From these, the following compounds were selected: $\text{Na}[\text{Mo}_3\text{O}_2(\text{OAc})_9]$, $\text{Cs}_2[\text{Mo}_3\text{O}_4(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_3]$, $(\text{NH}_4)_5[\text{Mo}_3\text{O}_4\text{F}_9]$. NH_4F . H_2O , $[\text{Mo}_3\text{S}_4(\text{aq})_9]^{4+}$, $[\text{Mo}_4\text{S}_4(\text{aq})]^{6+}$, $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4$. However, due to the difficulties in preparing

$\text{Mo}_3\text{S}_4(\text{aq})_9^{4+}$ and $\text{Mo}_4\text{S}_4(\text{aq})_6^{6+}$ and because of their low yield, other related alternatives were prepared, namely $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9]3\text{KCN}\cdot 4\text{H}_2\text{O}$ and $\text{Mo}_4\text{S}_4(\text{dte})_6\cdot \text{C}_7\text{H}_8$ (see Chapter Four for discussion).

1.6 Pillared Clays

It has been known for a long time that intercalation of smectite clays (pillaring) can occur naturally. However intercalation of large ions into layered clays may lead to the formation of new phases with zeolitic properties such as high porous structure and large intracrystalline surface area which markedly improve the diffusive and sorptive properties of the host clay. Table 1.12 shows examples of organic and inorganic cations intercalated in clays and the properties of the prepared pillared clays.

Table 1.12. Intercalation of Cations Into Clay.

Intercalating Cation	Free Interlayer Spacing, Å	Decomposition Temp., °C	Reference
R_4N^+	4-4.5	250	169-171
[1,4-diazabicyclo[2.2.2]-octane] $^{2+}$	5	527	172,173
$[ML_3]^{2+}$ (M = Fe, Ni; L = phenanthroline, bipyridyl)	8	350	174
Polynuclear oxycations of Al and Zr	6-10	500	175-180
$[Si(acac)_3]^+$	3	>500	181,182
$M_6Cl_{12}^{2+,3+}$ (M = Nb, Ti)	19.9	400	183

Chapter 2

Experimental

2.1 Preparation of the Conventional and Allyl Molybdenum Catalysts

2.1.1 Conventionally Impregnated Catalysts

These catalysts were prepared according to the literature method (184) using the conventional two steps impregnation procedure. This technique involves mulling the appropriate additives in aqueous solution with $\gamma\text{-Al}_2\text{O}_3$ or $\text{F}^-/\gamma\text{-Al}_2\text{O}_3$ prepared from α -alumina monohydrate (Catapal SB) by the gel impregnation technique. The bulk composition and the surface acidity of the prepared catalysts are summarized in Table 3.1.

2.1.2 Anchored Molybdenum Allyl Catalysts

(a) The support ($\gamma\text{-Al}_2\text{O}_3$). It was prepared by drying α -alumina monohydrate (Catapal SB) at 105°C for 15 h followed by calcination at 500°C for 4 h. The support was then oxidized in pure oxygen at 550°C for 1.5 h followed by evacuation at the same temperature for 1 h and kept under vacuum at room temperature until required for use. After this treatment, $\gamma\text{-Al}_2\text{O}_3$ has, on average, 2 OH groups per $100\text{\AA}^2$ (31).

(b) Molybdenum allyl complexes. The complexes $\text{Mo}(\pi\text{-C}_3\text{H}_5)_4$ and $\text{Mo}_2(\pi\text{-C}_3\text{H}_5)_4$ were prepared according to literature methods (27,185,186) from allylmagnesium chloride and molybdenum pentachloride (187,188).

(c) Anchoring of $\text{Mo}(\pi\text{-C}_3\text{H}_5)_4$ or $\text{Mo}_2(\pi\text{-C}_3\text{H}_5)_4$ on $\gamma\text{-Al}_2\text{O}_3$ (25,27,189, 190). To a suspension of $\gamma\text{-Al}_2\text{O}_3$ (from step (a) above) in dry and deoxygenated pentane, an excess of the complex in the same solvent was added and the reaction mixture was stirred for 30-60 min. at 0°C . The product was then filtered, washed three times with pentane, twice with diethyl ether, followed by drying under vacuum at room temperature for 1 h.

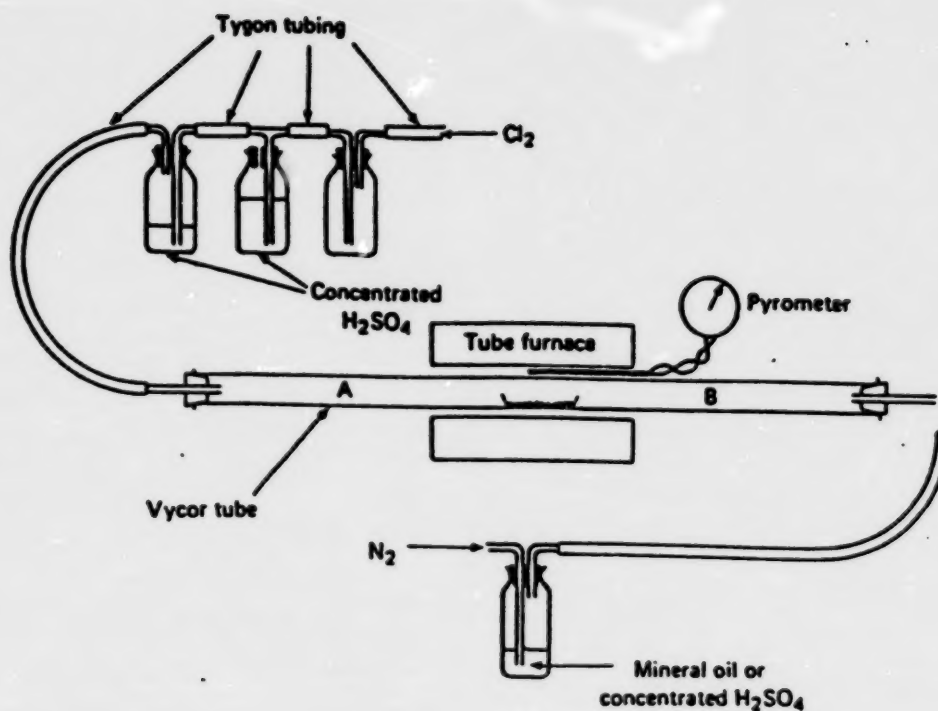
(d) Chemical treatment of the molybdenum allyl catalysts. Both catalysts were first reduced under a stream of H_2 gas at a rate of 30 ml min^{-1} at $600^\circ C$ followed by oxidation with O_2 gas flowing at the same rate as above (room temperature) for 2 h and higher temperature ($300^\circ C$ for the monomeric and $400^\circ C$ for the dimeric catalysts) for another 2 h to give catalysts K-4 and K-8 respectively (Table 3.1). Preparation of the allyl complexes is summarized in Scheme 3.1 whereas the preparation and chemical treatment of the catalysts derived from them are shown in Scheme 3.2A & B.

2.2 Preparation of Supported Molybdenum Cluster Catalysts

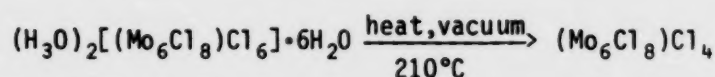
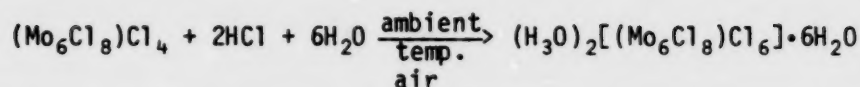
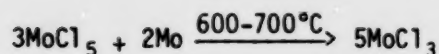
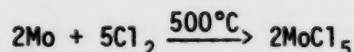
2.2.1 Synthesis of the Selected Cluster Compounds

(a) $Na[Mo_3O_2(OAc)_9]$ and $[Mo_3O_2(OAc)_6(H_2O)(OH)_2] \cdot 16H_2O$ (94). A mixture of freshly recrystallized sodium molybdate dihydrate (5 g), tungsten hexacarbonyl (10 g), and degassed acetic anhydride (300 ml) was refluxed under N_2 for 4 h. The cooled mixture was filtered to give red precipitate of $Na[Mo_3O_2(OAc)_9]$ which was then washed with ether and dried under vacuum. The compound was purified by dissolving in methanol, filtered and the solvent was evaporated under vacuum. The resulted red precipitate was then pumped at $50-70^\circ C$ for 8 h. Yield = 80%. However, the compound $Mo_3O_2(OAc)_6(H_2O)(OH)_2 \cdot 16H_2O$ was easily obtained by the acid hydrolysis of the above compound in 0.1 M HCl overnight. Yield = 75%.

(b) $(H_3O)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ and $(Mo_6Cl_8)Cl_4$. These compounds were prepared by the well-established method reported by W.L. Jolly (191) using the apparatus shown in the diagram and according to the following reactions.

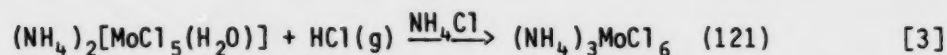
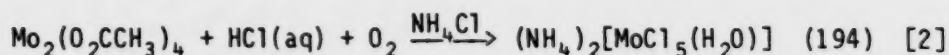
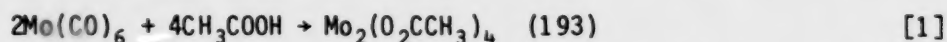


Apparatus for the Preparation of $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4$



(c) $\text{Cs}_2[\text{Mo}_3\text{O}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_3 \cdot 4\text{H}_2\text{O} \cdot 1/2\text{H}_2\text{C}_2\text{O}_4$. A solution of Mo(IV) prepared by modifying Murmann's method (192) as follows.

A stoichiometric amounts of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (1.81 g, 7.5 mM) and $(\text{NH}_4)_3\text{MoCl}_6$ (5.445 g), 15 mM), prepared according to equations 1-3, in 1.2 M HCl at 80-90°C under nitrogen for 2 h (equation 4).



The resulting Mo(IV) solution was then cooled to room temperature and passed through a Dowex 50Wx2 cation exchange column (H-form, 25 cm long and 5.4 cm diameter). The column was washed with 250 ml of 0.5 M HCl and 750 ml of 1.0 M HCl to remove the yellow Mo(V) impurities. To prepare the above oxalate complex, the dark red layer of Mo(IV), which remained at the top of the

column, was then eluted with 500 ml of 0.5 M oxalic acid (103). 2 g of CsCl was added to the eluate and upon evaporation to 20 ml and treatment with 60 ml of acetone in an ice-bath, a purple precipitate was obtained. It was separated by filtration and purified by dissolving in 20 ml of degassed water and cooled in an ice-bath. The slow addition of acetone (60 ml) to this solution precipitated a red-purple microcrystalline product. Yield: crude product = 5 g, pure product = 4 g (which is about 60% of the total Mo used).

(d) $(\text{NH}_4)_5[\text{Mo}_3\text{O}_4\text{F}_9]\cdot\text{NH}_4\text{F}\cdot\text{H}_2\text{O}$. A new method was developed for the preparation of this cluster compound using less expensive chemicals and containers compared to Müller's method (121). The dark red layer of Mo(IV) obtained according to the above procedure as in (c) above was then eluted with 4-5 M HCl and evaporated to about 20 ml.

The mixture was then transferred to a 100 ml Nalgene flask and 10 ml of 49% HF was added followed by 4 g of NH_4F . Excess acetone was added and the mixture was then cooled in an ice-bath for 1 h. The resultant precipitate (the title compound mixed with excess NH_4F) was filtered and dried. Excess NH_4F was then removed by treatment with water as the cluster compound $(\text{NH}_4)_5[\text{Mo}_3\text{O}_4\text{F}_9]\cdot\text{NH}_4\text{F}\cdot\text{H}_2\text{O}$ is insoluble in water.

(e) $\text{Mo}_4\text{S}_4[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_6\cdot\text{C}_7\text{H}_8$.

(i) Preparation of the dithiocarbamate ligand (195). 48 ml (60.8 g, 0.8 mol) of CS_2 was added dropwise to a cooled (0-5°C) and stirred solution of 82.7 ml (58.5 g, 0.8 mol) of diethylamine in 400 ml of distilled water followed by a dropwise addition of 320 ml of 10% NaOH solution (32 g, 0.8 mol). When a clear solution was obtained, 80 g of $\text{K}_2\text{S}_2\text{O}_8$ in 1 l of distilled water was slowly added while keeping the temperature of the reaction mixture at (0-5°C). The mixture was stirred for an extra 30 min. The

solid was filtered, washed with water and dried under vacuum. It was then recrystallized from hot ethanol. The yield was about 70%.

(ii) Preparation of the cluster compound. This cluster compound was prepared by modifying the previously reported method (142). A mixture of 26.4 g (0.1 mol) of hexacarbonylmolybdenum and 44.4 g (0.15 mol) of N,N,N',N'-tetraethylthiuram disulfide in 700 ml of dry and deoxygenated toluene was refluxed in the dark under nitrogen for 72 h. The reaction mixture was cooled to room temperature and filtered in air. The resulting blue-black precipitate was then washed several times with acetone and dried under vacuum. The yield was about 17 g (50% based on molybdenum).

(f) $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9] \cdot 3\text{KCN} \cdot 4\text{H}_2\text{O}$.

(i) Preparation of the starting materials.

(1) Ammonium polysulfide solution, $(\text{NH}_4)_2\text{S}_x$ (112). This solution was prepared by passing H_2S gas for 4 h into a mixture of 200 ml of water, 500 ml of concentrated ammonium hydroxide and 180 g of sulfur.

(2) $(\text{NH}_4)_2(\text{Mo}_3\text{S}_{13}) \cdot 1/2\text{H}_2\text{O}$ (112,196). To a solution of ammonium molybdate tetrahydrate, (22 g) in 100 ml of warm water, ammonium polysulfide solution, prepared as above, was added and the mixture was heated for 16 h in a one-neck round bottom flask covered with a clock glass. When cooled to room temperature, the reaction mixture was filtered. The resulting dark-red precipitate was washed with water, ethanol and dried under vacuum. The impure product was then stirred in 5 portions (100 ml each) of CS_2 and filtered to dissolve all the sulfur impurities rendering the compound $(\text{NH}_4)_2(\text{Mo}_3\text{S}_{13}) \cdot 1/2\text{H}_2\text{O}$ pure.

(ii) Preparation of the cluster compound (86). Upon addition of excess KCN (82 g) to a suspension of $(\text{NH}_4)_2(\text{Mo}_3\text{S}_{13}) \cdot 1/2\text{H}_2\text{O}$ (12 g) in 400 ml

of water, a deep-green solution of $[\text{Mo}_3\text{S}_4(\text{CN})_9]^{5-}$ was soon obtained. After stirring for 1 h, the mixture was filtered. Ethanol was added to the filtrate until clouding occurred. After filtration of the precipitate, the process was repeated. The filtrate was then treated with more ethanol until an oily product appeared on the bottom of the flask. After several hours, the green precipitate was filtered, washed with ethanol and dried under vacuum. Yield (11 g), 60% based on molybdenum.

2.2.2 Preparation of Supported Molybdenum Cluster Compounds

Each supported molybdenum cluster compound was prepared by mixing certain weight of $\gamma\text{-Al}_2\text{O}_3$ with the required weight of the molybdenum cluster compound dissolved in a suitable solvent. The mixture was then stirred for 5 min. followed by drying in an oven in air at about 50°C for several hours with occasional stirring. The details of the quantities and kind of solvents are shown in Table 2.1

2.2.3 Preparation of Fluorided Supported Molybdenum Cluster Catalysts

These catalysts were prepared by impregnating them with an appropriate amount of ammonium fluoride such that there were one fluoride atom per ten aluminum atoms in each catalyst. The quantities of each catalyst, ammonium fluoride and water used in the above preparation were as follows:

Code	Precursor	Weight of Precursor (mg)	Weight of Ammonium Fluoride (mg)	Volume of Water (ml)
Cat-3/F	Cat-3	200.0	14.0	1.0
Cat-6/F	Cat-6	200.0	12.5	1.0

Table 2.1. Preparation of the Supported Molybdenum
Cluster Compounds on γ -Alumina.

Code	Cluster Compound*	Weight of Compound (g)	Weight of γ -Al ₂ O ₃ (g)	Solvent (ml)
Cat-1	Na[Mo ₃ O ₂ (OAc) ₉] 1	0.796	5.020	15 Methanol
Cat-3	(H ₃ O) ₂ [(Mo ₆ Cl ₈)Cl ₆]•6H ₂ O 3	0.515	5.035	5 H ₂ O + 10 Acetone
Cat-4	Cs ₂ [Mo ₃ O ₄ (ox) ₃ (H ₂ O) ₃]• 4H ₂ O• ¹ / ₂ H ₂ C ₂ O ₄ 4	0.896	5.006	10 H ₂ O + 1 HCl
Cat-5	(NH ₄) ₅ [Mo ₃ O ₄ F ₉]•NH ₄ F•H ₂ O 5	0.614	5.020	30 (1:1) HCl:H ₂ O
Cat-6	Mo ₄ S ₄ (Et ₂ dtc) ₆ •C ₇ H ₈ 6	0.974	5.014	25 Warm CHCl ₃
Cat-7	K ₅ [Mo ₃ S ₄ (CN) ₉]•3KCN•4H ₂ O 7	0.971	5.005	10 H ₂ O

* Compound 2 is [Mo₃O₂(OAc)₆(H₂O)(OH)₂]•16H₂O.

OAc = acetato ion, ox = oxalato ion, Et₂dtc = diethyldithiocarbamate ion.

2.2.4 Preparation of Cat-31, Cat-32 and Cat-33

(a) Preparation of Cat-31. Cat-3 (10 g) was added to a solution of 0.552 g (1.96 mMol) of cobalt nitrate hexahydrate, $[\text{Co}(\text{NO}_3)_2] \cdot 6\text{H}_2\text{O}$, in 5 ml of water. The mixture was stirred for 5 min. and dried in air in an oven at 50–60°C for several hours.

(b) Preparation of Cat-32.

(i) Fluorided γ -alumina ($\text{F}/\gamma\text{-Al}_2\text{O}_3$). To 400 g Boehmite (A100H) was added 130 ml of H_2O and mulled for 3–5 min. Then 467 ml of H_2O was added and the mixture was again mulled for a further 3–5 min. Finally, 21.8 g (0.59 mole) of NH_4F in 30 ml of H_2O was added, the beaker which was containing NH_4F was washed with 5 ml of H_2O and the wash was added to the alumina mixture. The slurry was then mulled for another 5 min., dried overnight in air in an oven at 105°C (15 h). Samples of the dried mixture (100 g each) was calcined as mentioned in section 2.1.2 (a).

(ii) Cat-32. $\text{F}/\gamma\text{-Al}_2\text{O}_3$ (20 g) was added to a solution of 2.06 g (0.845 mMol) of $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6] \cdot 6\text{H}_2\text{O}$. The mixture was stirred for 5 min. and dried in air in an oven at 50–60°C for several hours.

(c) Preparation of Cat-33. Cat-32 (9.93 g) was added to solution of 0.504 g (1.794 mMol) of cobalt nitrate hexahydrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in 5 ml of water. The mixture was stirred for 5 min. and dried in air in an oven at 50–60°C for several hours.

2.3 Preparation of Pillared Clays "Intercalation of Niobium and Tantalum Cluster Cations in Montmorillonite"

2.3.1 Preparation of Na-Montmorillonite

A clay sample was suspended in doubly distilled water (1.0 wt %) and allowed to sediment for 24 h to precipitate carbonate and other dense

impurities. The suspended clay fraction was then decanted and the clay was collected by centrifugation (1 h, 3000 rpm). To ensure complete exchange to the sodium form, it was resuspended in 1.0 M NaCl for 24 h followed by centrifugation and washing free of excess chloride with distilled water. The Na-montmorillonite was then freeze-dried for 24 h.

2.3.2 Preparation of Intercalated Montmorillonite

A solution of 1 g $M_6Cl_{14} \cdot 8H_2O$ ($M = Nb, Ta$) (218) in 250 ml of ethanol was added to 5 g of Na-montmorillonite. The mixture was stirred at ambient temperature for 18 h. The resulting product was then centrifuged and washed repeatedly with 20 ml portions of ethanol until free from excess metal cluster compound. The pale green pillared clay was then freeze-dried for 24 h.

During the preparation of the pillared clay, all manipulation were carried out while attempting to minimize contact with atmospheric oxygen.

The amounts of Nb and Ta clusters intercalated into 5 g of clay, estimated approximately by subtracting the amount that remains in solution after intercalation from that originally used, are 0.15 g and 0.19 g respectively. This is equivalent to 1.4% Nb and 2.3% Ta respectively.

2.4 The Catalyst Testing

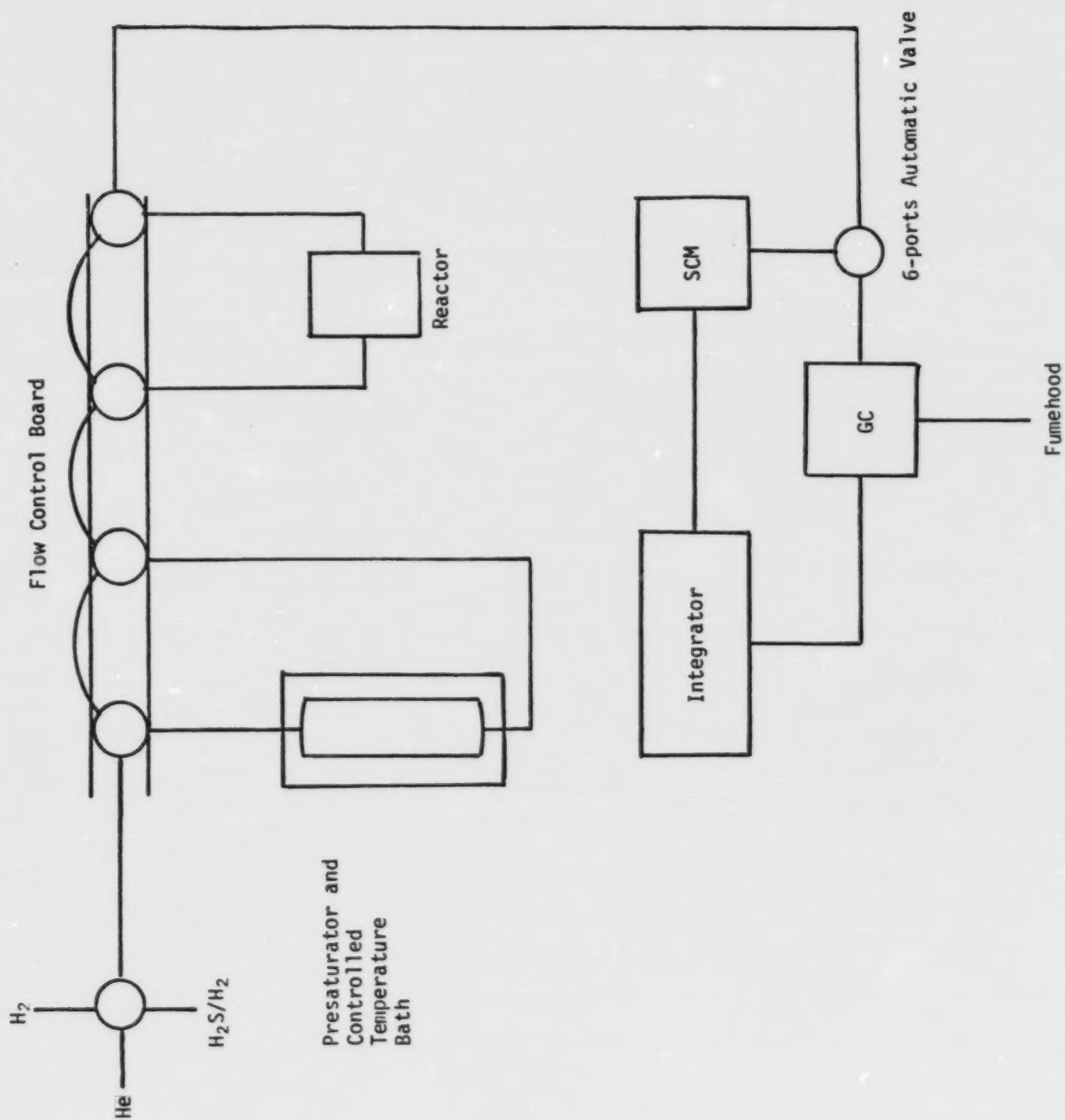
2.4.1 Testing on Model Compound

(a) Cumene hydrocracking. The catalyst testing was carried out in a continuous-flow fixed-bed bench-top stainless steel microreactor with an inner diameter of 15 mm. The catalyst (equivalent to 0.15 g of $MoO_3/\gamma-Al_2O_3$ catalyst, 120-200 mesh) was supported between two quartz wool plugs. It was reduced by heating to 500°C under a flow (30 ml/min.) of hydrogen and left at

that temperature for 1.5 h. The cumene (reactant) was held at a constant temperature (20°C) in a presaturator and passed through the reactor in a stream of hydrogen at 30 ml/min. The reactor temperature was 400°C $\pm$ 1%. The reaction products were analyzed by a gas chromatograph connected to the outlet of the reactor using H₂ as the carrier gas. Cumene hydrocracking products were analyzed at 100°C on (6 ft., 1/8 in.) 5% Di-isodecylphthalate +5% Bentone 34 on 60-80 mesh chromosorb W. The complete testing reactor system is shown in the diagram and the calculation procedure is outlined in section 2.4.3.

(b) Thiophene hydrodesulfurization, HDS (hydrogenolysis). Thiophene HDS was carried out on the same flow reactor system used for cumene hydrocracking. The catalysts (see section 2.4.1 (a) for the amount and mesh size of the catalyst) was sulfided by heating to 500°C under a flow (30 ml/min.) of 10% H₂S/H₂ and left at that temperature for 1.5 h. Excess H₂S was flushed out from the reactor with H₂ gas prior to testing. The thiophene (reactant) was held at a constant temperature (14°C) in a presaturator and passed through the reactor in a stream of H₂ at 30 ml/min. The reactor temperature was 400°C $\pm$ 1%. The hydrodesulfurization products were analysed by a gas chromatograph at 60°C on (10 m, 530 m) Carbowax 20 M using H₂ as the carrier gas. The calculation procedure is outlined in section 2.4.3.

(c) Propene hydrogenation. The procedure for hydrogenating of propene is similar to that of cumene hydrocracking with the following modifications: (i) the propene (reactant) was held at an ambient temperature (21°C); (ii) the propene/hydrogen ratio was 4/26 ml/min.; (iii) the GC column used was Porasil B, 80-100 mesh kept at 60°C; and (iv) the presaturator was replaced by a propene gas cylinder.



Catalyst Testing Network

2.4.2 Hydrotreatment of Syncrude Coker Gas Oil (SCGO)

The hydrotreatment of SCGO involved the following stages:

(a) Sulfidation of the catalyst. 1.0 g of the catalyst and 2 ml of CS_2 were added to the pressure reactor. The sealing ring around the stirrer was sprayed with tetrafluoroethylene (TFE) and the stirrer was bolted down to 50 ft. lb. The reactor was pressure tested for leaks with 500 psi argon gas. The argon was vented out and 1000 psi of hydrogen gas was added. The reactor temperature was then set at 450°C for 3 h.

(b) Redistribution. The redistribution of the sulfide formed during the sulfidation process was carried out for 3 h as follows: the reaction gases from the sulfidation process were vented out of the reactor which was then flushed 3 times with 500 psi of argon gas, followed by the introduction of a 1000 psi of hydrogen gas. The reactor temperature was then kept at 450°C throughout the duration of the experiment.

(c) SCGO hydrotreatment. The reaction gas from the redistribution experiment was vented out and the reactor was flushed 3 times with 500 psi of argon gas. The stirrer was unbolted and removed. 25 g of Syncrude Coker Gas Oil (SCGO) was added while a flow of argon gas was blowing over the catalyst to prevent any contact with air. The sealing ring was again coated with PTFE and the stirrer was bolted down to 50 ft. lb. The vessel was pressure-tested for leaks with 500 psi of argon gas. The gas was vented out and 1500 psi of hydrogen gas was introduced. The reactor temperature was kept at 410°C for 3 h.

2.4.3 Calculation Procedures

(a) Cumene hydrocracking.

$$\text{Conversion \%} = \frac{\Sigma(A_i \times SFi) - \text{cumene}}{\Sigma(A_i + SFi)} \times 100$$

$$\text{Yield \%} = \frac{A_i \times SFi}{\Sigma(A_i \times SFi) - \text{cumene}} \times \text{Conv. \%}$$

A_i = amount of aromatic product i

SFi = molar sensitivity factor of the detector for aromatic i

Cumene = amount of cumene ($SF = 1.000$)

(b) Thiophene hydrodesulfurization.

$$\text{Conversion \%} = \frac{T_{in} - T_{out}}{T_{in}}$$

T_{in} = amount of thiophene entered the reactor

T_{out} = amount of thiophene left the reactor

or more accurately:

$$\text{Conversion \%} = \frac{P_1 - P_2}{P_1} \times 100$$

P_1 = % of thiophene in the sample before the catalytic reaction

P_2 = % of thiophene in the product after the catalytic reaction

(c) Propene hydrogenation. The percent conversion was calculated following the methods used for the hydrodesulfurization process.

(d) SCGO hydrotreatment.

$$^{\circ}\text{API} = \frac{141.5}{\text{sp. gr (15.6}^{\circ}\text{C)}} - 131.5$$

2.5 Physical Measurements

2.5.1 Infrared Spectra

The infrared spectra of the pure compounds were recorded as 2% KBr disks on a Nicolet 8000 interferometer at a resolution of 2 cm^{-1} in the region $4000\text{--}400\text{ cm}^{-1}$ and on a Perkin-Elmer 467 Grating Infrared Spectrometer in the range $4000\text{--}300\text{ cm}^{-1}$. The spectra of the treated molybdenum allyl catalyst were obtained on the same interferometer using 20-25 mg of the sample pressed in 13 mm self-supported wafer. The pretreatment of these wafers involved evacuation for 1 h at room temperature followed by oxidation (cleaning) in O_2 gas ($1/2\text{ atm}$) at 500°C for 4 h and evacuation at the same temperature for another 1 h. After the spectra were recorded, pyridine vapor (17 Torr) was adsorbed on the catalyst for 30 min. at 100°C spectra were again recorded after pyridine desorption for 1 h at 100°C and also after H_2O vapor (15 Torr) was added (1 min., 100°C) and desorbed (30 min., 100°C) to enhance the intensity of the Brønsted-pyridine bands. However, the spectra of the supported molybdenum cluster compounds were recorded on the above interferometer as 10-20% KBr disks without further treatment.

2.5.2 Raman Spectra

These spectra were recorded on a Jarell-Ash Raman spectrometer model 25-100 at a resolution of 8 cm^{-1} . Samples were treated in a similar procedure as the infrared spectra.

2.5.3 Electronic Spectroscopy

Electronic spectral measurements were performed in solution and in the solid state; as KBr disks and/or as a nujol mull on a Cary 219 spectrophotometer.

2.5.4 Differential Scanning Calorimetry

This study was conducted on a Perkin-Elmer model DSC-2 differential scanning calorimeter at a scan rate of 10°C/min.

2.5.5 Density

The densities of the hydrotreated and untreated gas oil were measured using a PAAR digital density meter model DMA 40.

2.5.6 Viscosity

The viscosity was obtained using a Brookfield digital viscometer model Ex-100.

2.5.7 Sulfur Content

The sulfur analysis was carried out on:

- (a) Princeton gamma-tech X-ray fluorescence sulfur analyzer model-100 using standards contains 0.94% and 4.48% sulfur.
- (b) Perkin-Elmer 240 B Elemental Analyzer using S-benzylthiuronium chloride as standard.

2.5.8 Elemental Analysis

Elemental analysis for Cl, Al and Mo were carried out by Guelph Chemical Laboratories.

Chapter 3

Results

Table 3.1. Bulk Compositions and Approximate Surface Acidity of Conventional Co-Mo/Al₂O₃ and Related Catalysts, and those obtained from Allyl-Molybdenum Complexes.

Catalyst	Additive			Acidity IR Intensity ^c cm ⁻¹	
	F ^a	CoO ^b	MoO ₃ ^b	1540 (B)	1450 (L)
γ-Al ₂ O ₃	0	0	0	0 ^d	7.7 ^d
F ⁻ /γ-Al ₂ O ₃	1	0	0	0.05 ^d	12.7 ^d
KJ-1	0	0	15	5.6 ^d	15.0 ^d
KJ-2	0	3	15	2.9 ^d	15.9 ^d
MRF-1	1	0	15	- ^f	- ^f
MRF-2	1	3	15	5.4 ^d	10.4 ^d
K-4 ^g	0	0	0.75-1.5	0 ^e	14.0 ^e
K-8 ^g	0	0	0.3-1.5	0 ^e	11.0 ^e

^a Number of F atoms per 11 Al atoms.

^b Weight %.

^c The IR intensities of adsorbed species are corrected for the weight of the sample; the units are absorbance per gram of catalyst. B, Brønsted; L, Lewis acidity.

^d These intensities are taken from Boorman and Kydd results reported in reference (184).

^e This work.

^f Not yet determined.

^g Prepared from monomeric and dimeric molybdenum allyl complexes respectively.

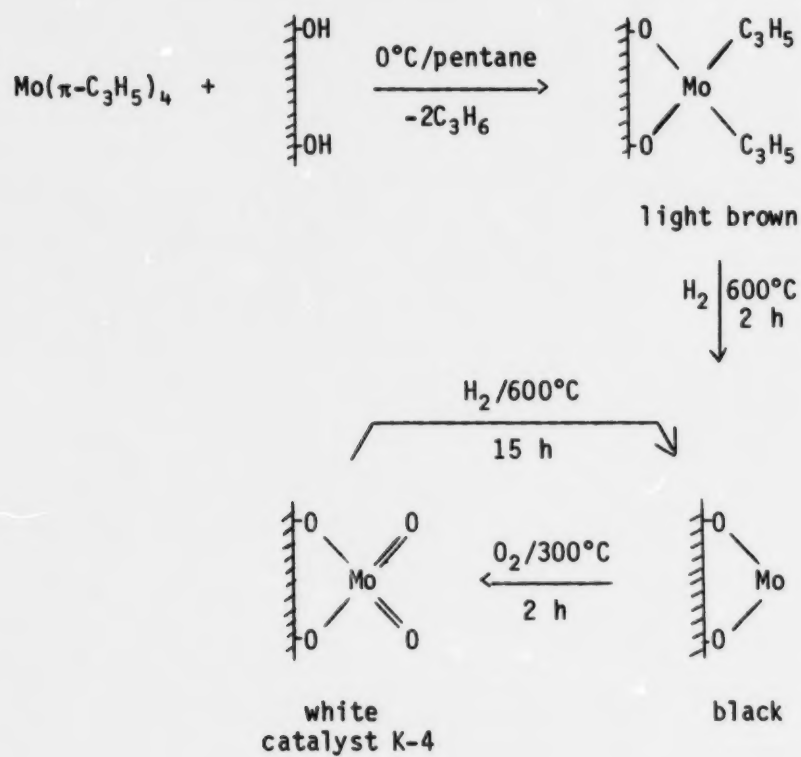
Scheme 3.1. Preparation of Molybdenum Allyl Complexes.

1. $\text{C}_3\text{H}_5\text{Cl} + \text{Mg} \xrightarrow[12 \text{ h, diethyl ether}]{-15^\circ\text{C (ethylene glycol bath)}} \text{C}_3\text{H}_5\text{MgCl} \text{ (187,188)}$
 0.25 mole 2 moles
 (large excess)

2. $4\text{C}_3\text{H}_5\text{MgCl} + \text{MoCl}_5 \xrightarrow[\text{diethyl ether}]{<-20^\circ\text{C, 1.5 h}} \xrightarrow[\text{pentane}]{-40^\circ\text{C, 20 h}} \xrightarrow[\text{pentane}]{-30^\circ\text{C}} \text{Mo}(\pi\text{-C}_3\text{H}_5)_4$
 0.096 mole 0.02 mole Yield 25%

3. $\text{C}_3\text{H}_5\text{MgCl} + \text{MoCl}_5 \xrightarrow[\text{diethyl ether}]{20^\circ\text{C, 6 h}} \xrightarrow[\text{pentane}]{\text{dry ice/acetone bath}} \text{Mo}_2(\pi\text{-C}_3\text{H}_5)_4$
 0.106 mole 0.019 mole Yield 25%

Scheme 3.2A. Anchoring of $\text{Mo}(\pi\text{-C}_3\text{H}_5)_4$ on $\gamma\text{-Al}_2\text{O}_3$.



Scheme 3.2B. Anchoring of $\text{Mo}_2(\pi\text{-C}_3\text{H}_5)_4$ on $\gamma\text{-Al}_2\text{O}_3$.

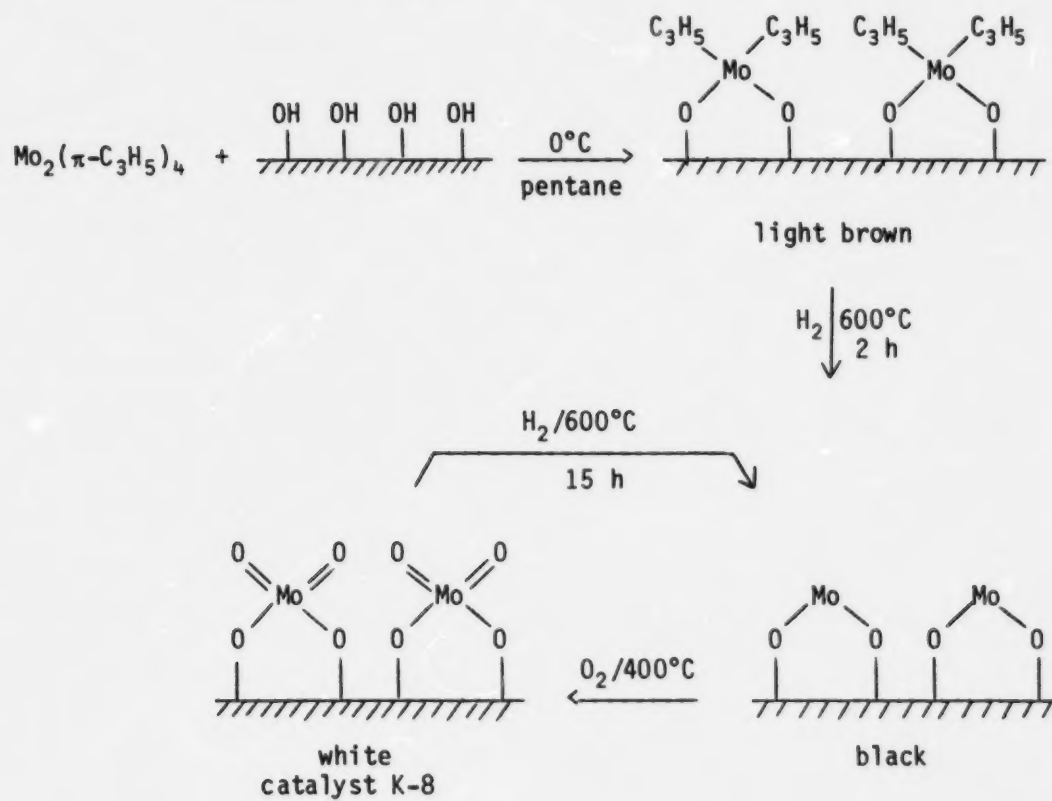


Table 3.2. Infrared Spectroscopy of the Cluster Compounds.

3.2.1 $\text{Na}[\text{Mo}_3\text{O}_2(\text{OAc})_9]$

Important Band Positions, cm^{-1}	Tentative (197-200) Assignments
3010 m } 2985 m } 2932 m }	$\nu(\text{CH})$
1719 s,b } 1641 s,b } 1551 s,b } 1444 s,b } 1367 s,b } 1283 s,b }	$\nu(\text{COO})$
686 s } 640 s } 595 s }	$\rho(\text{COO})$
527 m	$\nu(\text{Mo}-\text{O}_{\text{OAc}})$
472 m	$\nu(\text{Mo}-\text{O}_{\text{C}})$

3.2.2 $[\text{Mo}_3\text{O}_2(\text{OAc})_6(\text{H}_2\text{O})(\text{OH})_2] \cdot 16\text{H}_2\text{O}$

3585 m	coordinated OH and/or H_2O
3550-3200 s,br	lattice H_2O
1650-1620 m,br	$\rho(\text{OH})$
1525 s } 1450 s } 1415 sh } 1355 m }	$\nu(\text{COO})$
690 s } 650 s } 592 s }	$\rho(\text{COO})$

3.2.3 $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6] \cdot 6\text{H}_2\text{O}$

3600-3150 s,br	$\nu(\text{H}_2\text{O})$
1615 s	$\rho(\text{H}_2\text{O})$
365 w	$\nu(\text{Mo-Cl})$
335 sh	
330 s	
317 sh	

3.2.4 $\text{Cs}_2[\text{Mo}_3\text{O}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_3] \cdot 4\text{H}_2\text{O} \cdot 1/2\text{H}_2\text{C}_2\text{O}_4$

3600-3370	lattice H_2O
3215 s,br	$\nu(\text{OH})$, coordinated H_2O
1700 s	$\nu(\text{C=O})$
1671 s	
1606 sh	
1386 s	$\nu(\text{C-O})$
1322 m	
1257 m	
782 s	$\nu(\text{Mo-O}_b)$
750 s	
721 s	
537 m	$\nu(\text{Mo-O}_{\text{ox}})$
472 s	$\nu(\text{Mo-O}_c)$

3.2.5 $(\text{NH}_4)_5[\text{Mo}_3\text{O}_4\text{F}_9] \cdot \text{NH}_4\text{F} \cdot \text{H}_2\text{O}$

3413 s,br	lattice H_2O
3151 s,br	$\nu(\text{NH})$
1617 s	$\rho(\text{H}_2\text{O})$
1400 s	$\nu(\text{NH})$
780 s	$\nu(\text{Mo-O}_b) + \nu(\text{Mo-F})$
746 s	
714 s	
427 s	$\nu(\text{Mo-O}_c)$

3.2.6 $\text{Mo}_4\text{S}_4[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_6 \cdot \text{C}_7\text{H}_8$

2986 s	}	v(CH)
2927 s		
2889 m		
1493 s		v(R-N C)
991 s		v _s (CS)
568 s	}	v _a (CS)
559 sh		
360 s	}	v(MoS)
345 sh		
320 sh		

3.2.7 $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9] \cdot 3\text{KCN} \cdot 4\text{H}_2\text{O}$

3600-3200 s, br	lattice H_2O
2118 s	v(CN)
1613 s	$\rho(\text{H}_2\text{O})$
367 s	Mo-S _b
337 s	

Table 3.3. Electronic Spectroscopy of the Cluster Compounds.

3.3.1 $\text{Na}[\text{Mo}_3\text{O}_2(\text{OAc})_9]$

solution		conc. mmol/l		ϵ		Transmittance (KBr disks)	
nm	kk	1	2	1	2	nm	kk
524	19.08	1.15	1.06	190	200	520	19.23
440	22.73	1.15	1.06	280	300	440	22.73
308	32.47	0.19	0.18	7150	7550		

3.3.2 $[\text{Mo}_3\text{O}_2(\text{OAc})_6(\text{H}_2\text{O})(\text{OH})_2] \cdot 16\text{H}_2\text{O}$

505	19.80	0.15	300	500	20.00
425	23.53	0.15	230	420	23.81

3.3.3 $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6] \cdot 6\text{H}_2\text{O}$

348	28.74	0.35	2285	350	28.57
304	32.89	0.35	2885	300	33.33

3.3.4 $\text{Cs}_2[\text{Mo}_3\text{O}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_3] \cdot 4\text{H}_2\text{O} \cdot 1/2\text{H}_2\text{C}_2\text{O}_4$

540 sh	18.52 sh	0.455	440	540	18.52
380 sh	26.32 sh	0.455	1600	400	25.00
240	41.67	0.06	29300	248	40.32

3.3.5 $(\text{NH}_4)_5[\text{Mo}_3\text{O}_4\text{F}_9] \cdot \text{NH}_4\text{F} \cdot \text{H}_2\text{O}$

532	18.79	1.16	240	560	17.86
312 sh	32.05 sh	0.29	1240	400	25.00

3.3.6 $\text{Mo}_4\text{S}_4[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_6 \cdot \text{C}_7\text{H}_8$

732 sh	13.66 sh	0.17	500	740	
565	17.70	0.17	3822	580	
420 sh	23.81 sh	0.04	2250	410	
350 sh	28.57 sh	0.04	11000	360	
264	37.88	very dilute			

3.3.7 $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9] \cdot 3\text{KCN} \cdot 4\text{H}_2\text{O}$

608	16.45	0.15	460	618	16.18
460 sh	21.74 sh	0.15	930		
376	26.60	0.15	6250	380	26.32
332	30.12	0.15	5600	324	30.86
280 sh	35.71 sh	0.05	1400		
240	41.67	0.05	25600		
208	48.08	0.05	37200		

Table 3.4. Raman Spectroscopy of the Cluster Compounds.

3.4.1 $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6] \cdot 6\text{H}_2\text{O}$

Band Positions cm^{-1}	Tentative Assignments
319 s	Mo-Cl
250 s	
228	$\nu(\text{Mo-Mo})$ (97)
200	
176	

3.4.2 $(\text{NH}_4)_5[\text{Mo}_3\text{O}_4\text{F}_9] \cdot \text{NH}_4\text{F} \cdot \text{H}_2\text{O}$

152 m	
146 sh	v(Mo-Mo)
140 s	

Table 3.5. Differential Scanning Calorimetry of the Cluster Compounds.

3.5.1 $\text{Na}[\text{Mo}_3\text{O}_2(\text{OAc})_9]$

Weight (mg)	Transformation Temp. Peak, °K	Assignment
13.1	380 w,br (endo)	adsorbed H_2O
	507 s (endo)	decomposition (-OAc)
	572 s (endo)	further decomposition

3.5.2 $[\text{Mo}_3\text{O}_2(\text{oAc})_6(\text{H}_2\text{O})(\text{OH})_2] \cdot 16\text{H}_2\text{O}$

8.5	440 s (endo)	lattice H_2O
	480 s (endo)	coordinated H_2O and/or OH
	513 s (endo)	further decomposition

3.5.3 $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6] \cdot 6\text{H}_2\text{O}$

21.9	345 w,br (endo)	adsorbed H_2O
	377 s (endo)	lattice H_2O
	475 s,br (endo)	H_2O from the cation and HCl from the cation and anion

3.5.4 $\text{Cs}_2[\text{Mo}_3\text{O}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_3] \cdot 4\text{H}_2\text{O} \cdot 1/2\text{H}_2\text{C}_2\text{O}_4$

17.7	390 s,br (endo)	adsorbed H_2O + lattice H_2O
	400 sh (endo)	+ oxalic acid sublimation
	650 s,br (endo)	decomposition

3.5.5 $(\text{NH}_4)_5[\text{Mo}_3\text{O}_4\text{F}_9] \cdot \text{NH}_4\text{F} \cdot \text{H}_2\text{O}$

16.6	390 s,br (endo)	adsorbed H_2O + lattice H_2O
	643 m,br (endo)	+ NH_4F
	720 vs (endo)	$\text{NH}_4\text{F} \cdot \text{HF}$ decomposition

3.5.6 $\text{Mo}_4\text{S}_4[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_6 \cdot \text{C}_7\text{H}_8$

17.2	490 m	(endo)	toluene
	634 vs	(endo)	decomposition

3.5.7 $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9] \cdot 3\text{KCN} \cdot 4\text{H}_2\text{O}$

19.3	380 s,br	(endo)	adsorbed H_2O + lattice H_2O
	582 m,br	(exo)	decomposition
	626 m,br	(exo)	further decomposition

w, weak; m, medium; s, strong; vs, very strong; O_{Ac} , oxygen atom from the acetato ligand; O_{ox} , oxygen atom from the oxalato ligand; O_b , bridging oxygen; O_c , capping oxygen; ν_s , symmetric stretching; ν_a , asymmetric stretching.

Table 3.6. Solid State Electronic Spectroscopy
of Supported Mo-Cluster Compounds.

Supported Mo-Cluster Compound	Band Positions (nm)
Cat-1	510, 430
Cat-3	360
Cat-4	545, 400
Cat-5	560, 410
Cat-6	590, 410
Cat-7	610, 390

Description of Catalysts

Mo Cluster Impregnated on Support (see Table 3.9)

Cat-1	$\text{Na}[\text{Mo}_3\text{O}_2(\text{OAc})_9]$	see 3.3.1
Cat-3	$(\text{H}_3\text{O}^+)_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6] \cdot 6\text{H}_2\text{O}$	see 3.3.3
Cat-4	$\text{Cs}_2[\text{Mo}_3\text{O}_4(\text{ox})_3(\text{H}_2\text{O})_3] \cdot 4\text{H}_2\text{O}$	see 3.3.4
Cat-5	$(\text{NH}_4)_5[\text{Mo}_3\text{O}_4\text{F}_9]\text{NH}_4\text{F} \cdot \text{H}_2\text{O}$	see 3.3.5
Cat-6	$\text{Mo}_4\text{S}_4(\text{Et}_2\text{dtc})_6 \cdot \text{C}_7\text{H}_8$	see 3.3.6
Cat-7	$\text{Ks}[\text{Mo}_3\text{S}_4(\text{CN})_9]_3 \cdot \text{KCN} \cdot 4\text{H}_2\text{O}$	see 3.3.7

Table 3.7. Differential Scanning Calorimetry
of Supported Mo-Cluster Compounds.*

Supported Mo-Cluster Compound	Weight (mg)	Transformation Temp. Peak, K	Remarks
Cat-1	25.8	384 (endo) >400 (endo)	Adsorbed H ₂ O Gradual Decomposition
Cat-3	21.0	372 (endo) >473 (endo)	Adsorbed and Lattice H ₂ O Gradual Decomposition
Cat-4	23.4	394 (endo) >473 (endo)	Adsorbed and Lattice H ₂ O Gradual Decomposition
Cat-5	25.0	390 (endo) >473 (endo)	Adsorbed and Lattice H ₂ O Gradual Decomposition
Cat-6	16.8	>523 (endo)	Gradual Decomposition
Cat-7	14.6	370 (endo) >423 (exo)	Adsorbed and Lattice H ₂ O Gradual Decomposition

* Compare with Unsupported Data, 3.5.1-3.5.7

Table 3.8. Electronic Spectra of $\text{Nb}_6\text{Cl}_{12}^{2+}$ and $\text{Ta}_6\text{Cl}_{12}^{2+3+}$ in Solution, Solid State and Intercalated in Montmorillonite.

Literature (201)			This Work		
Intercalated Nb Cluster nm	Solid $\text{Nb}_6\text{Cl}_{12}^{2+}$ nm	Solution $\text{Nb}_6\text{Cl}_{12}^{2+}$ nm	Intercalated Nb Cluster nm	Solid $\text{Nb}_6\text{Cl}_{12}^{2+}$ nm	Solution $\text{Nb}_6\text{Cl}_{12}^{2+}$ nm
403	-	405	400	402	402

Intercalated Ta Cluster nm	Solid $\text{Ta}_6\text{Cl}_{12}^{2+}$ nm	Solution $\text{Ta}_6\text{Cl}_{12}^{2+}$ nm	Solution $\text{Ta}_6\text{Cl}_{12}^{3+}$ nm	Intercalated Ta Cluster nm	Solid $\text{Ta}_6\text{Cl}_{12}^{2+}$ nm	Solution $\text{Ta}_6\text{Cl}_{12}^{2+}$ nm	Solution $\text{Ta}_6\text{Cl}_{12}^{3+}$ nm
775	-	750	810	805	750	750	825
652	-	635	715	702	650	642	730
395	-	395	395	412	390	395	400

Table 3.9. Composition and Activity of Alumina-Supported Molybdenum Cluster Compounds Using Model Compounds.

Catalyst	Additives			Cumene Hydrocracking					Thiophene HDS	Propylene Hydrogenation		Precursor Compound
	F*	% CoO	% MoO ₃	% Conv.	% Yield					% Conversion	% Conversion	
					Benz.	EtB	Sty	g-Me Sty				
γ-Al ₂ O ₃	0.0	0.0	0.0	0.9	0.1	0.0	0.0	0.9	1.3	0.5		AlO(OH)
KJ-1	0.0	0.0	15.0	2.2	0.7	0.1	0.0	1.2	8.9	78.0		Ammonium molybdate
KJ-2	0.0	3.0	15.0	2.4	0.9	0.2	0.0	1.3	30.3	-		"
KJ-3	0.0	0.0	7.0	-	-	-	-	-	6.2	76.0		"
K-4	0.0	0.0	~1.0	1.1	0.2	0.0	0.0	0.9	1.3	-		Mo(κ-C ₃ H ₅) ₄
K-8	0.0	0.0	0.3-1.5	1.0	0.1	1.0	1.0	0.9	1.4	-		Mo ₂ (κ-C ₃ H ₅) ₄
MRF-1	1.0	0.0	15.0	37.5	34.7	1.0	1.0	0.8	8.9	-		Ammonium molybdate + F-
MRF-2	1.0	3.0	15.0	36.0	33.4	0.7	1.0	0.8	14.3	-		" + Co(NO ₃) ₂
Cat-1	0.0	0.0	6.8	1.3	0.1	0.1	0.0	1.1	5.1	30.5		Na[Mo ₃ O ₂ (OAc) ₃]
Cat-3	0.0	0.0	6.6	11.5	2.6	0.0	8.0	1.0	10.0	18.4		(H ₃ O ⁺) ₂ [(Mo ₆ Cl ₈)Cl ₆ ·6H ₂ O]
Cat-3F	1.0	0.0	6.6	65.5	59.9	0.0	5.7	0.0	-	-		" + F-
Cat-4	0.0	0.0	6.2	1.0	0.0	0.0	0.0	1.0	3.1	8.9		Cs ₂ [Mo ₃ O ₄ (ox) ₃ (H ₂ O) ₃]·4H ₂ O
Cat-5	0.0	0.0	7.1	10.3	8.5	0.0	0.6	1.0	5.1	21.8		(NH ₄) ₅ [Mo ₃ O ₄ F ₉]NH ₄ F·H ₂ O
Cat-6	0.0	0.0	6.3	1.6	0.4	0.0	0.0	1.2	1.0	6.1		Mo ₄ S ₄ (Et ₂ dtc) ₆ ·C ₇ H ₈
Cat-6F	1.0	0.0	6.3	9.3	8.5	0.0	0.0	0.9	-	-		" + F-
Cat-7	0.0	0.0	6.8	-	-	-	-	-	0.9	2.4		K ₅ [Mo ₃ S ₄ (CN) ₉]·3KCN·4H ₂ O
Cat-3	0.0	0.0	6.6	13.7	7.8	0.1	4.8	0.8	10.0	18.4		
Cat-31	0.0	1.4	6.6	8.5	4.3	0.3	3.0	1.0	42.0	25.2		
Cat-32	1.0	0.0	6.6	72.3	68.2	0.0	4.1	0.0	16.5	6.7		
Cat-33	1.0	1.3	6.6	65.0	61.7	0.0	3.3	0.0	17.0	10.6		

* Number of F atoms per 10 Al atoms.

Table 3.10. Hydrotreatment of Syncrude Coker Gas Oil (SCGO).

Catalyst	Composition			Weight of Catalyst (g)	Particle Size (mesh)	Weight of Feedstock (SCGO) (g)	Density	API Gravity	Viscosity Millipascal Sec 295 K	%S		Aromaticity ^c
	F ^a	Co ^b	Mo ^b							Dept. Services	ASR	
without treatment	-	-	-	-	-	-	0.9729	13.941	77.5	3.01	3.87	0.300
Blank	-	-	-	-	-	25.0	0.9547	16.714	11.6	-	3.26	0.338
MB-480	0	2.37	10.0	1.0	80-100	25.0	0.9013	25.495	5.2	-	0.338	0.314
MB-481	1	2.37	10.0	1.0	80-100	25.0	0.8677	31.575	3.1	-	0.08	0.204
MB-500	2	2.37	10.0	1.0	80-100	25.0	0.8745	30.307	2.7	-	0.11	0.336
MB-501	0.5	2.37	10.0	1.0	80-100	25.0	0.9040	24.872	-	-	0.45	0.296
Cat-3	0	0	4.0	1.0	100-120	24.3	0.8972	26.057	6.7	e	0.75 ^d	0.338
Cat-31	0	1.1	4.0	1.0	100-120	26.3	0.8848	28.265	6.1	0.0 ^e	0.25 ^d	0.238
Cat-33	1	1.0	4.0	1.07	100-120	25.5	0.8974	26.00	6.6	0.0 ^e	0.23 ^d	0.18

^a Number of F atoms per 10 Al atoms.^b Weight %.^c Aromatic carbon/total carbon.^d Measured immediately after the hydrotreatment experiment.^e Measured 3-4 weeks after the hydrotreatment experiment.

Table 3.11. Hydrodesulfurization of Thiophene on Nb and Ta Based Catalysts. The Support is Pretreated Na-Montmorillonite.

Catalyst*	Compound Used	% Metal	% Cl		% Conversion
			Calc.	Found	
Nb-1	$\text{Nb}_6\text{Cl}_{14} \cdot 8\text{H}_2\text{O}$	1.4	1.21	1.47	0.8
Ta-1	$\text{Ta}_6\text{Cl}_{14} \cdot 8\text{H}_2\text{O}$	2.3	1.10	1.32	1.0

* The weight of the catalyst is 0.15 g in which the metal additives were calculated as M_2O_5 .

Infrared Spectra of the Cluster Compounds and their
Prespective γ -Alumina-supported Clusters.

Figure 3.1. IR Spectrum of
 $\text{Na}[\text{Mo}_3\text{O}_2(\text{OAc})_9]$.

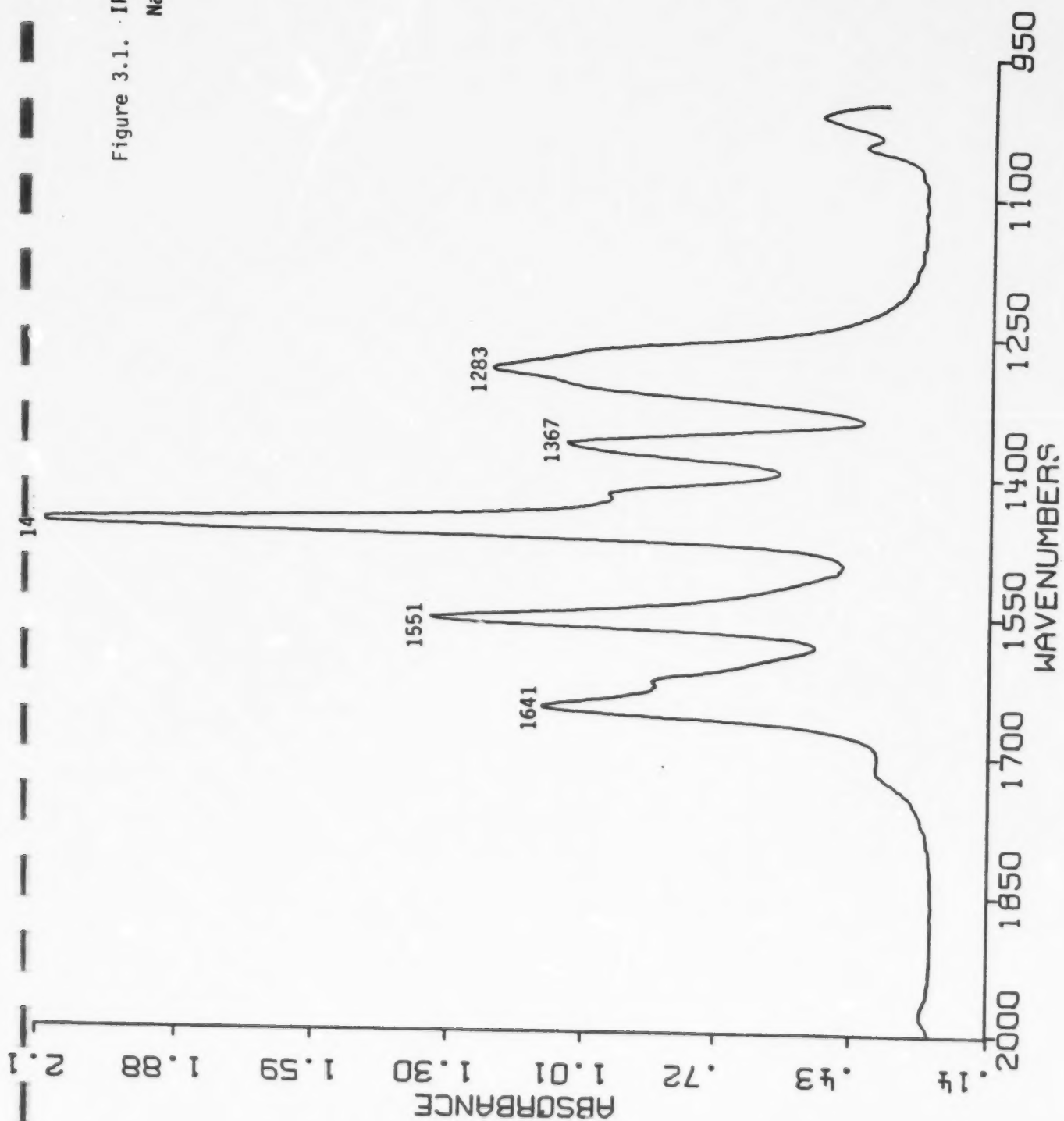


Figure 3.2. IR Spectrum of
 $[\text{Mo}_3\text{O}_2(\text{OAc})_6(\text{H}_2\text{O})_2] \cdot 16\text{H}_2\text{O}$.

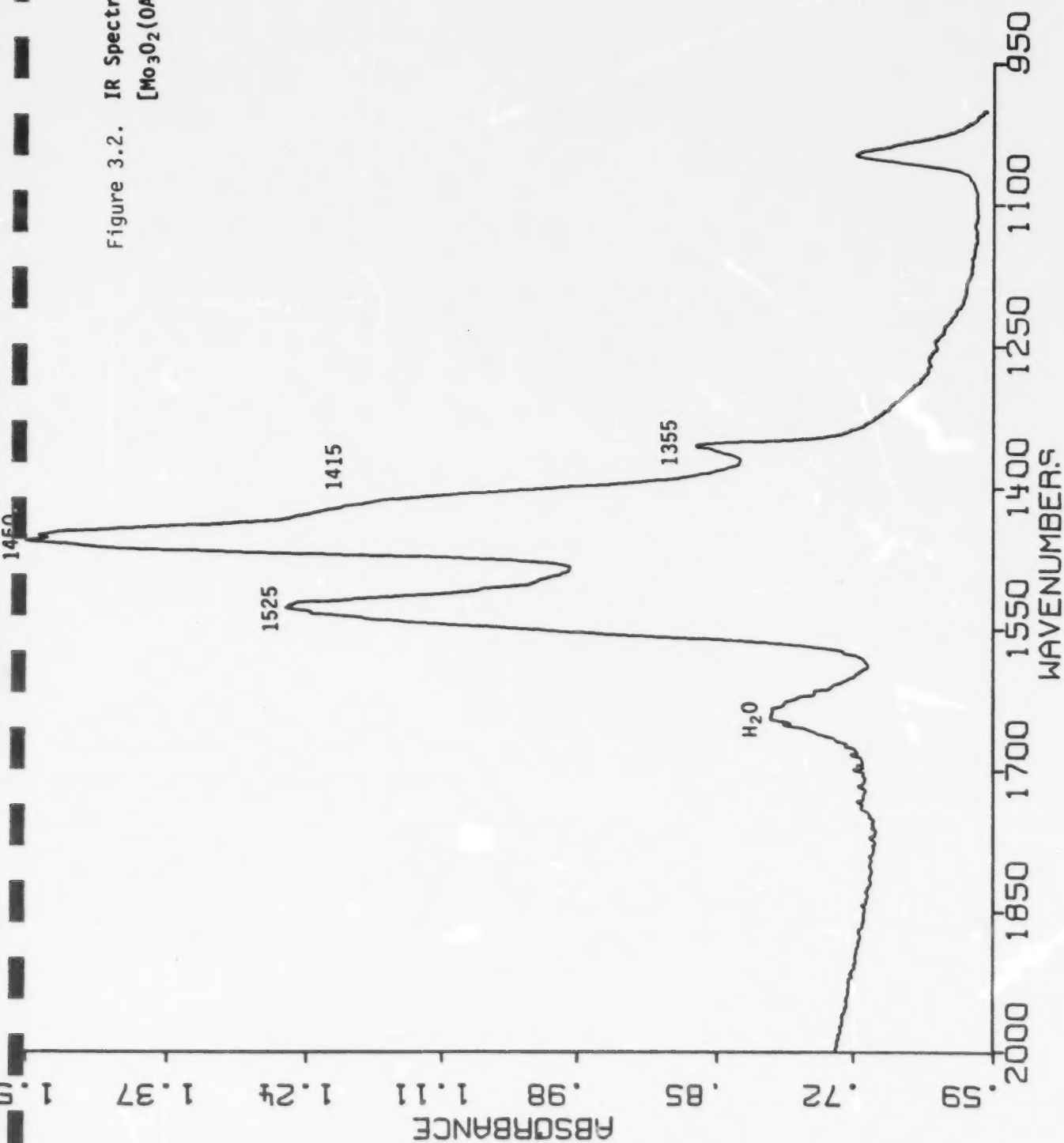


Figure 3.3. IR Spectrum of Cat-1.

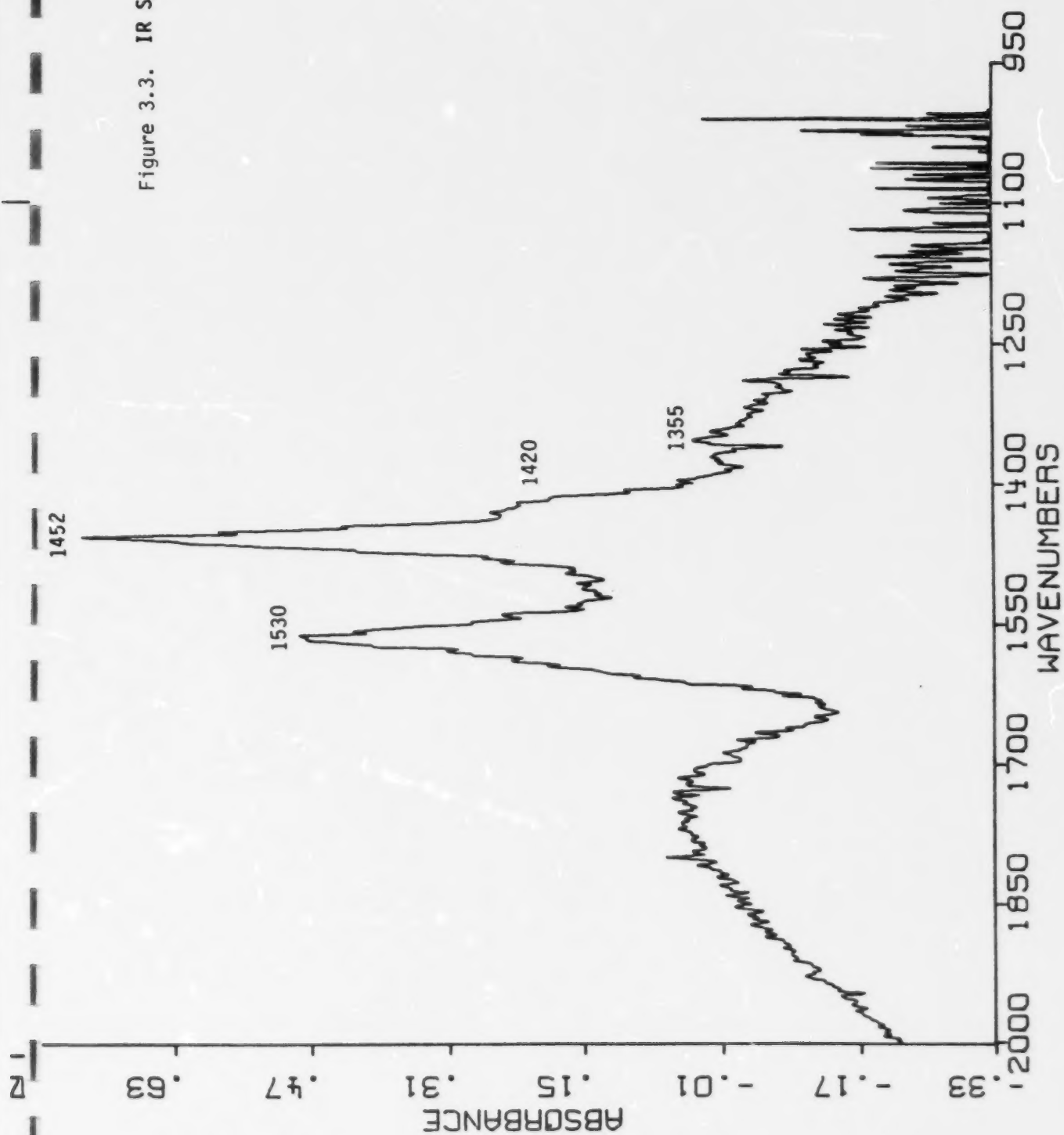
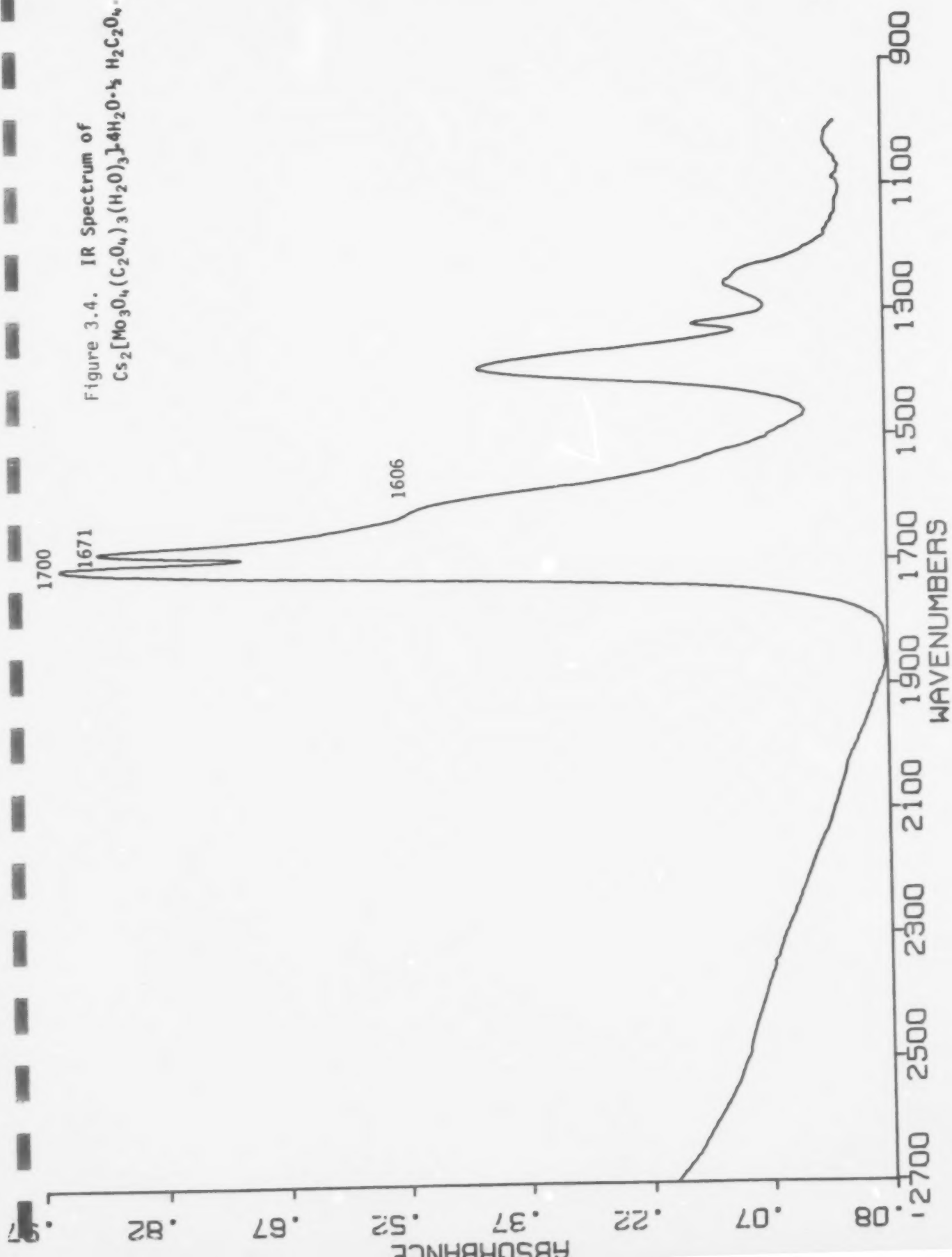


Figure 3.4. IR Spectrum of
 $\text{Cs}_2[\text{Mo}_3\text{O}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_3]_3 \cdot 4\text{H}_2\text{O} \cdot \frac{1}{2} \text{H}_2\text{C}_2\text{O}_4$



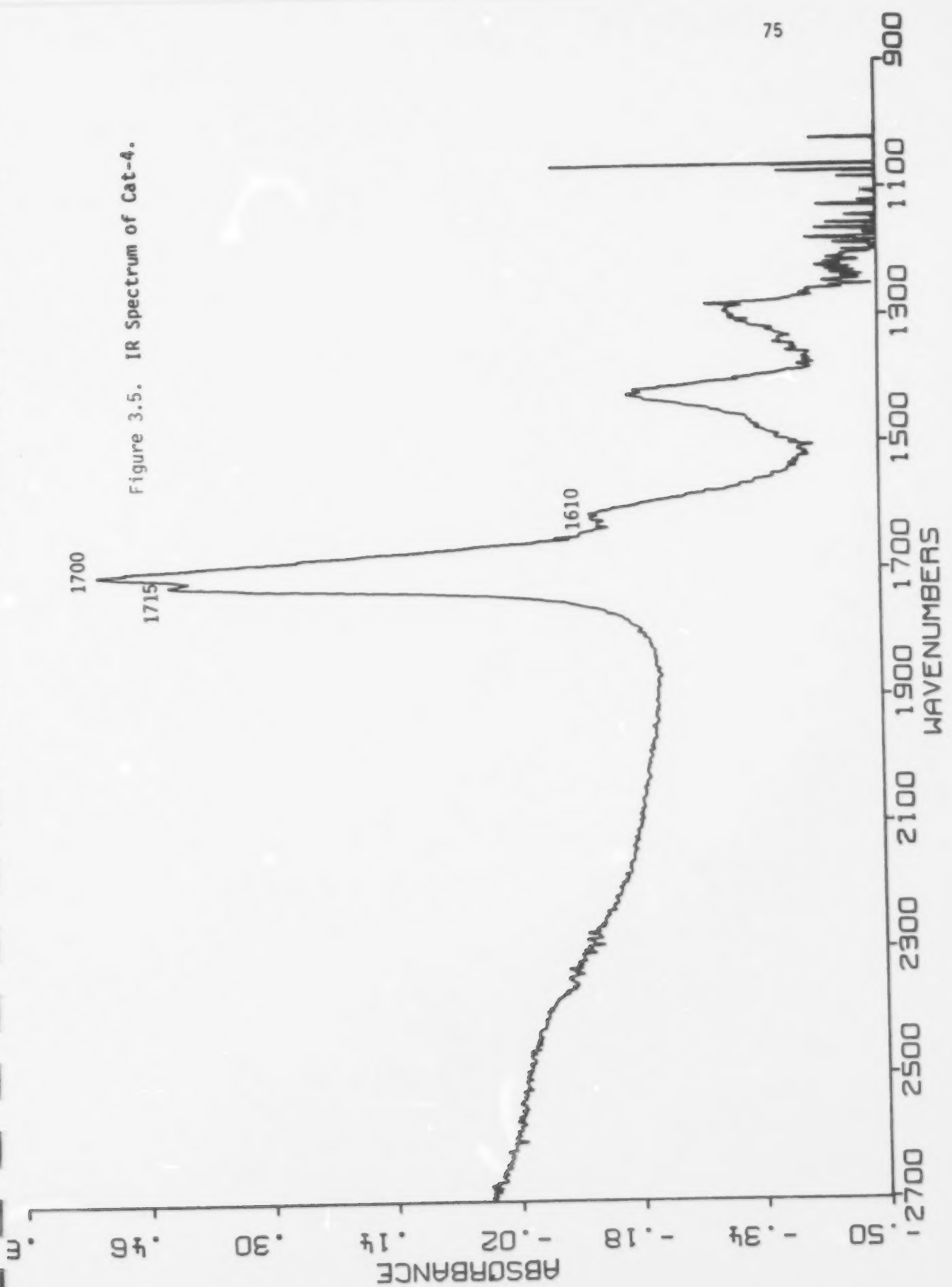


Figure 3.5. IR Spectrum of Cat-4.

Figure 3.6. IR Spectrum of
 $(\text{NH}_4)_5[\text{Mo}_3\text{O}_{14}\text{F}_9] \cdot \text{NH}_4\text{F} \cdot \text{H}_2\text{O}$.

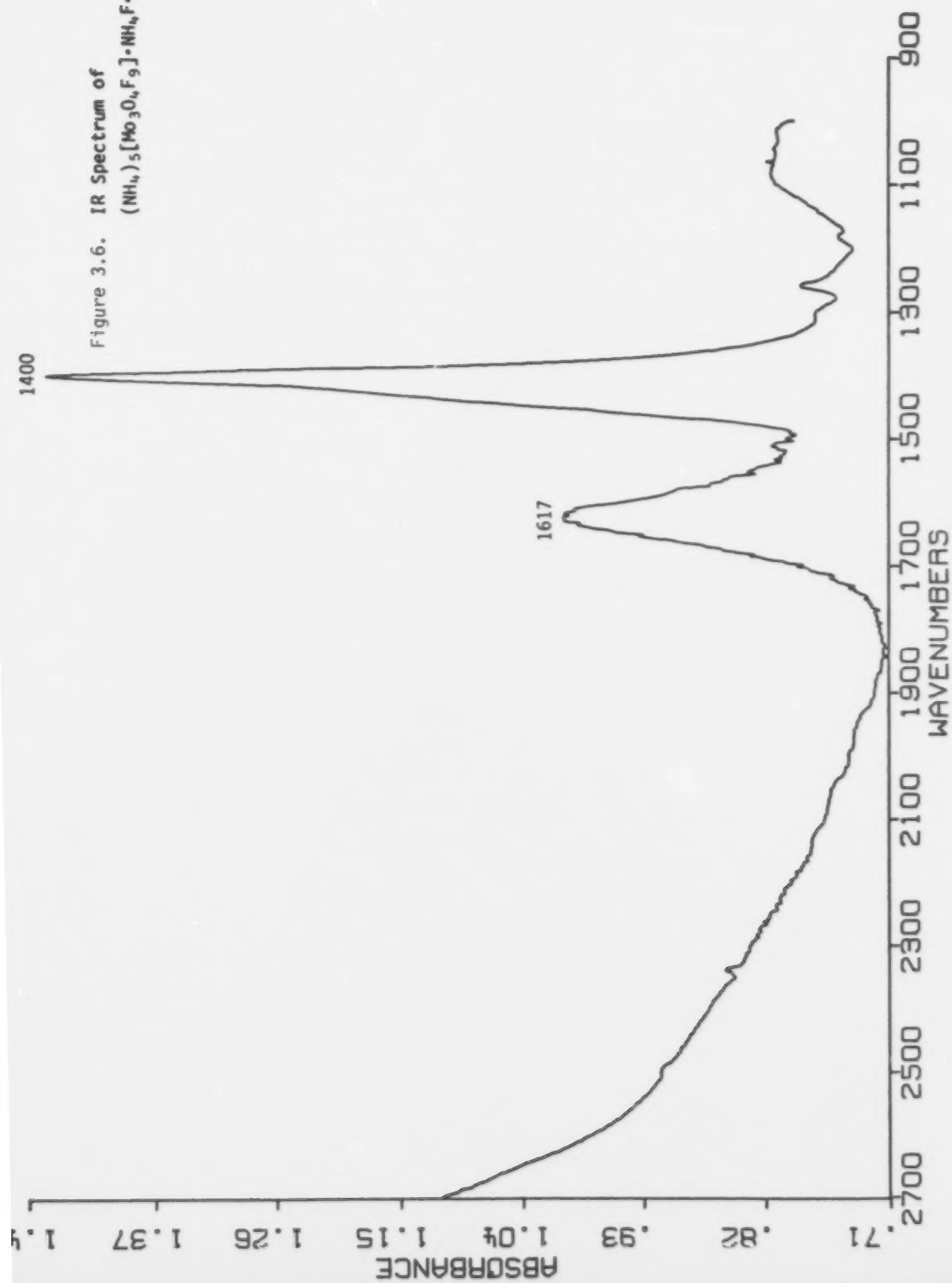


Figure 3.7. IR Spectrum of Cat-5.

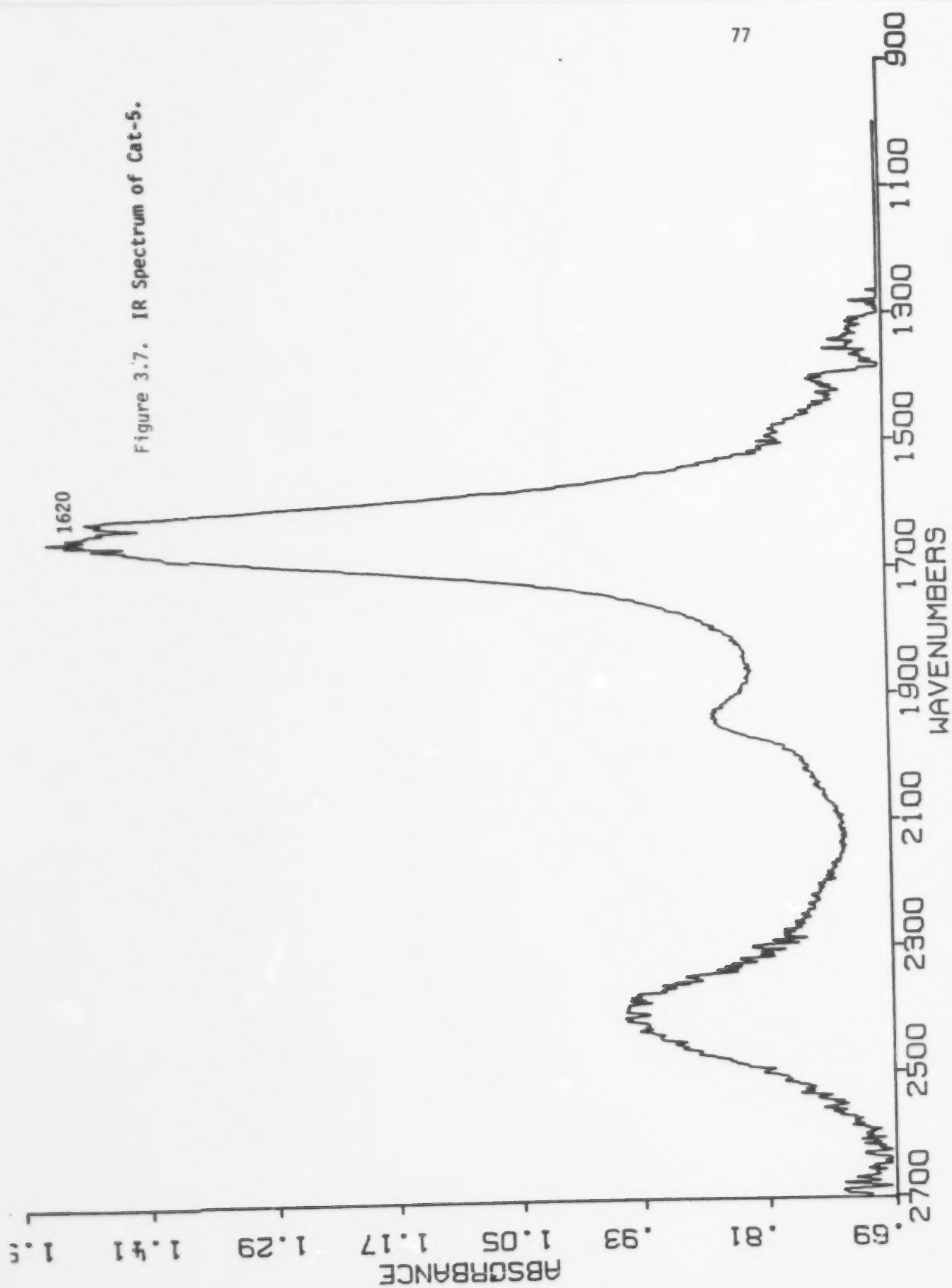


Figure 3.8. IR Spectrum of
 $\text{Mo}_4\text{S}_4(\text{Et}_2\text{dte})_6 \cdot \text{C}_7\text{H}_8$.

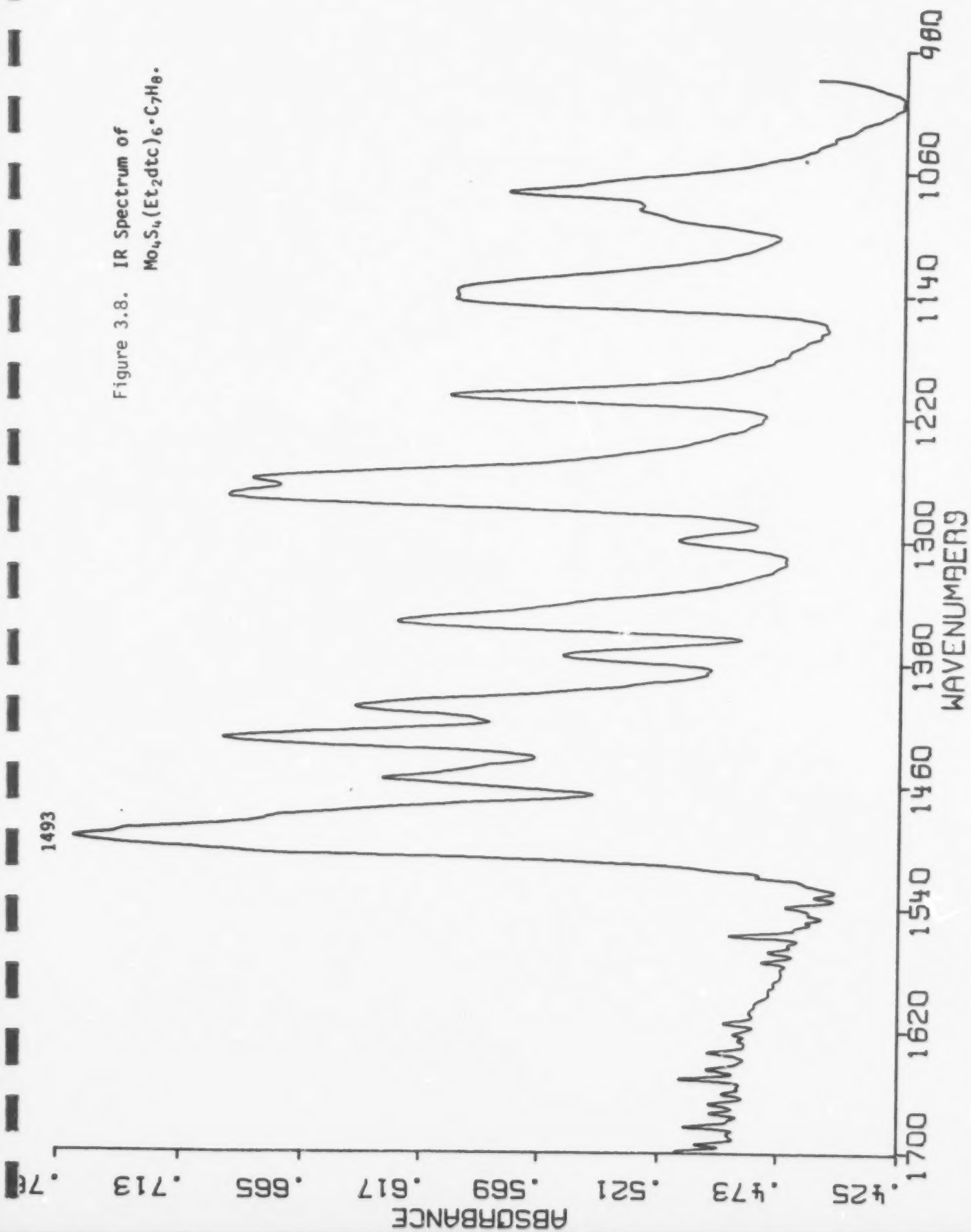


Figure 3.9. IR Spectrum of Cat-6.

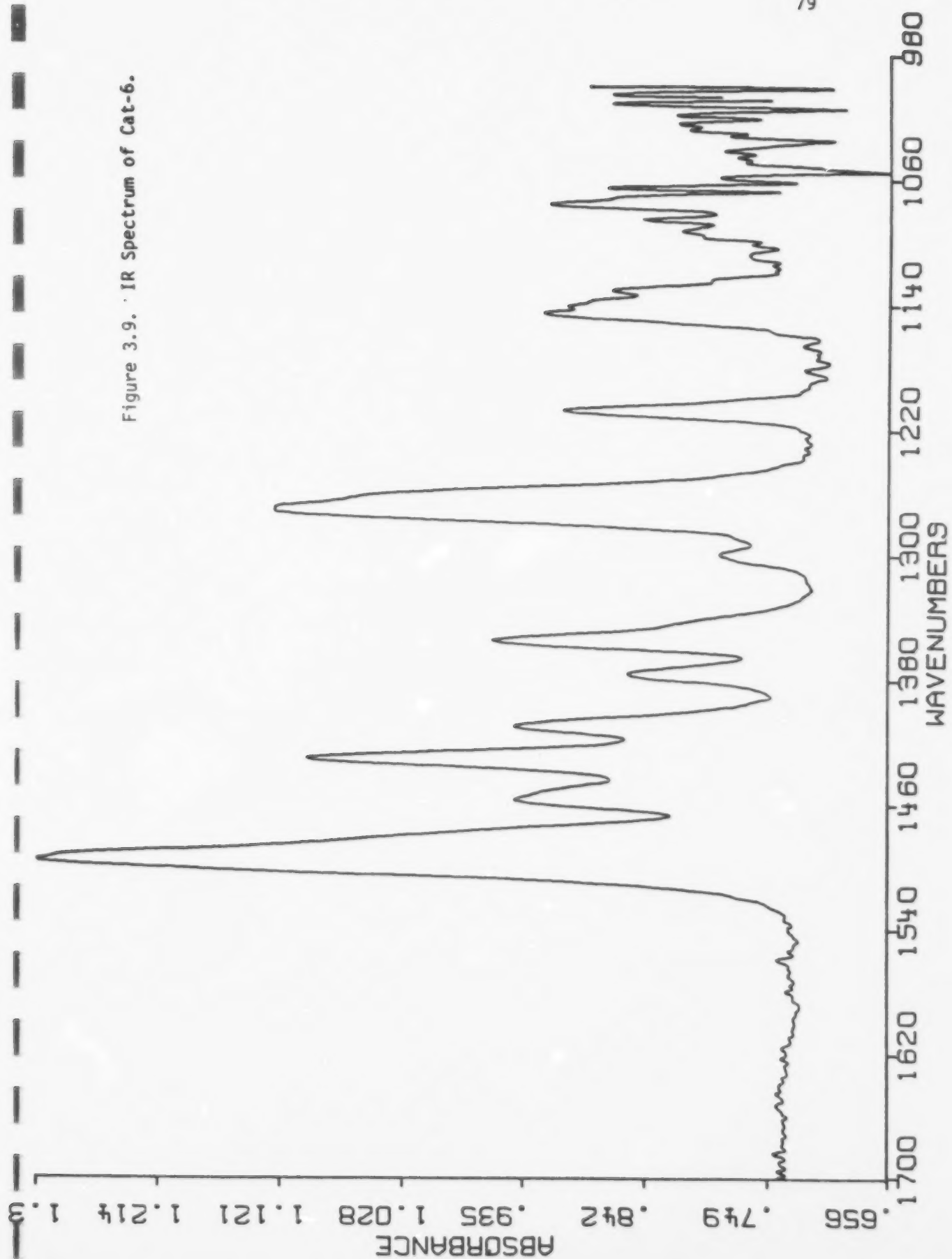


Figure 3.10. IR Spectrum of
 $K_5[Mo_3S_4(CN)_9] \cdot 3KCN \cdot 4H_2O$.

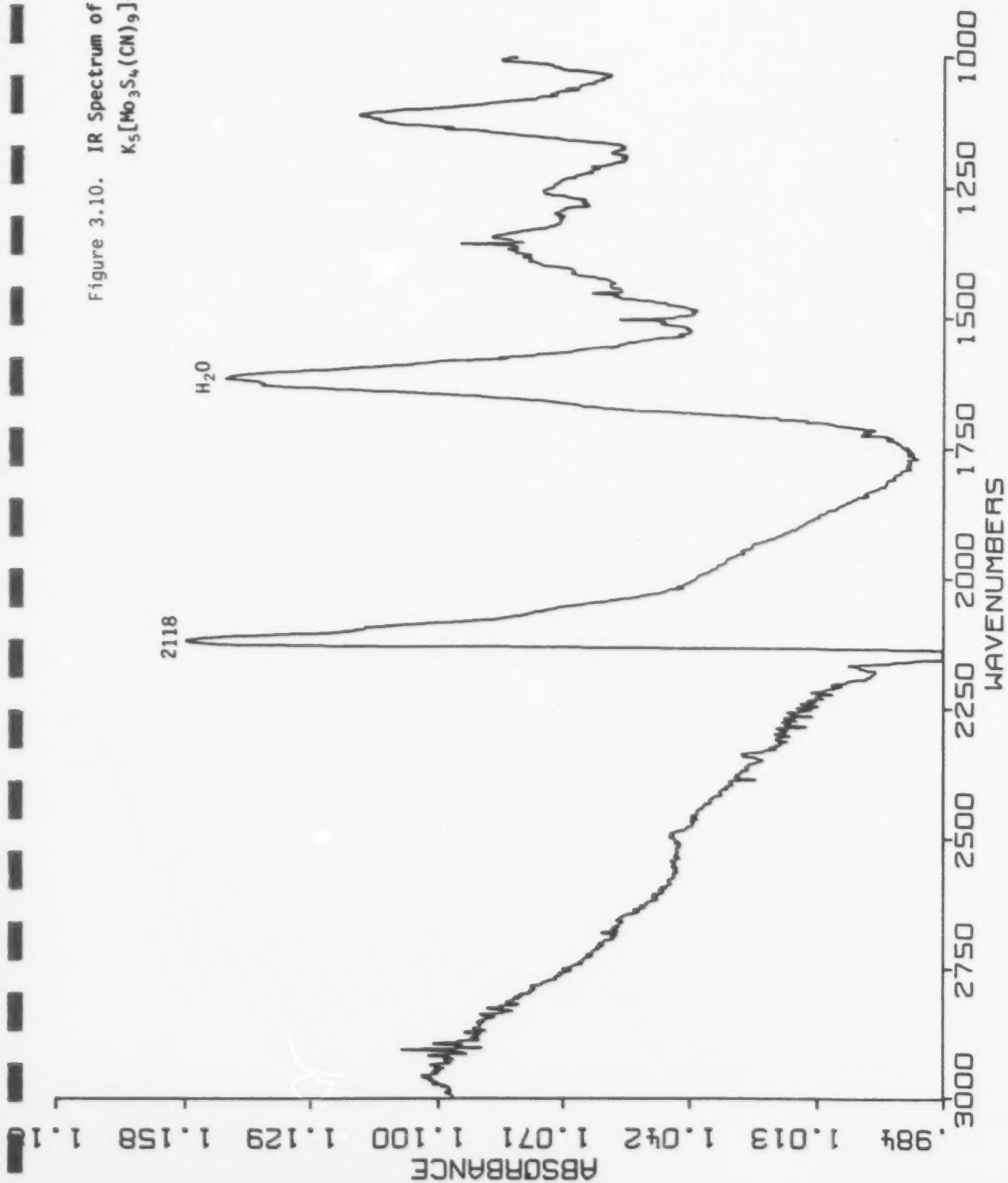
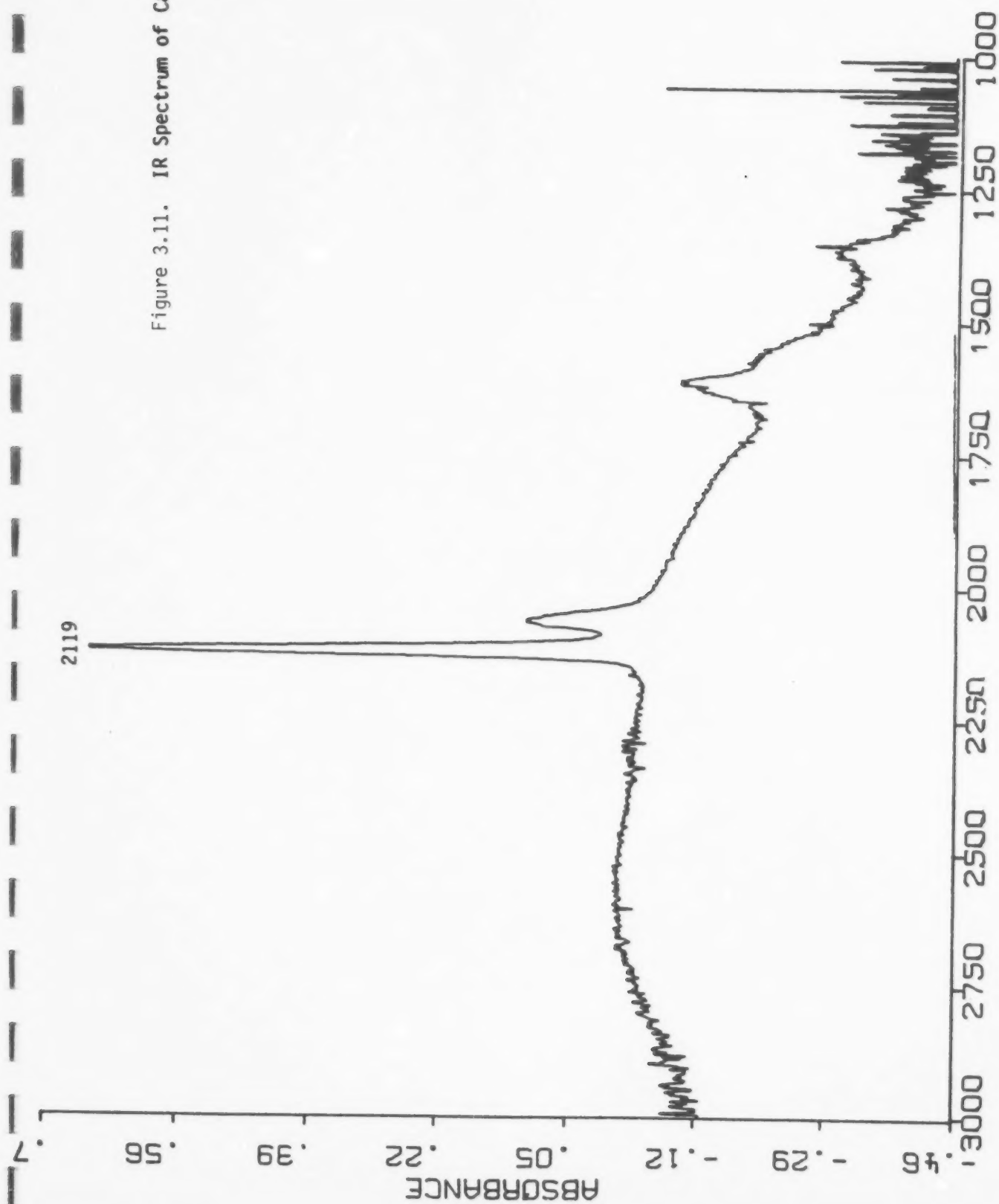


Figure 3.11. IR Spectrum of Cat-7.



Chapter 4

Discussion

4.1 Conventional and Molybdenum Allyl Catalysts

In a series of papers, Boorman, Brown, Kriz and Ternan (202,203), and Boorman, Kydd and co-workers (204,205) have reported the preparation, characterization, surface acidity measurements, and testing of a variety of conventionally prepared molybdenum catalysts supported on either $\gamma\text{-Al}_2\text{O}_3$ or fluorided $\gamma\text{-Al}_2\text{O}_3$. Bulk and surface concentrations of the components of the catalysts were estimated by elemental analysis and X-ray photoelectron spectroscopic study respectively. They have also reported the effect of contact time, activation temperature and reaction temperature on the cumene conversion. The optimum conditions for this type of reaction involved using an activation temperature of 500°C , a reaction temperature of 450°C , and a contact time of 450 g-h per mole of cumene. These authors also found that the followings have significant effects on the surface acidity and hence catalytic activities of these catalysts:

(a) Fluoride ions. They develop Brønsted sites on the surface of the support and intensify the Lewis acidity, a mechanism which involves the inductive effect due to the high electronegativity of the fluoride ions. The pyridinium band (PyH^+) appears at 1548 cm^{-1} in the IR spectrum of the catalyst, a manifestation of Brønsted acidity.

(b) MoO_3 . It develops Brønsted sites on the support, giving an ir band much more intense and at lower wavenumber (1541 cm^{-1}) than the comparable band for fluorided support. It also increases the Lewis acidity.

(c) CoO . It destroys the Brønsted acid sites on the $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts and leaves the Lewis acid sites unaffected.

(d) The sequence of impregnation. Catalysts prepared by the addition of Co and Mo compounds to fluorided $\gamma\text{-Al}_2\text{O}_3$ supports contain more Bronsted

sites than catalysts obtained by the addition of F^- ions to $Co-Mo/\gamma-Al_2O_3$ catalysts. We have repeated the preparation of some of these catalysts, namely, $\gamma-Al_2O_3$, $F^-/\gamma-Al_2O_3$, KJ-1, KJ-2, MRF-1 and MRF-2, their approximate bulk composition and surface acidity are summarized in Table 3.1.

Since 1978, Iwasawa et al. (26) have been working on the preparation, characterization, and a variety of activity-testing of catalysts obtained by supporting monomeric or dimeric molybdenum or chromium (206) allyl complexes on inorganic oxides supports. They studied the surface properties of these catalyst by many spectroscopic techniques such as IR, u.v. visible diffuse reflectance, X.P.S., photoluminescence, e.s.r., and EXAFS. These catalyst were tested for dehydrogenation of ethyl alcohol in the absence of oxygen (26), oxidation of ethyl alcohol with oxygen (26), partial oxidation of propene by O_2 and N_2O (29), selective ethane formation by carbon monoxide hydrogenation (207), olefin metathesis (28), olefin hydrogenation at low temperature (30), and photocatalytic oxidation of propane by oxygen (208).

We have repeated the preparation of these catalysts according to the equations shown in Scheme 3.1. Redox reactions with H_2 gas (reduction) and O_2 gas (oxidation) were also carried out and represented in Schemes 3.2A & B. We have also studied the surface acidity of these catalysts using FT-IR spectroscopic technique and attempted the study of their Laser Raman spectra (see Table 3.1, samples K-4 and K-8). The fixation process (209) obviously depends upon the nature of both the organometallic compound employed and the surface OH groups of the support, the population and distribution of the OH groups, the fixing temperature, and reaction time. The amount of Mo on alumina was estimated according to Iwasawa et al. results (27,31).

4.1.1 Spectroscopic Studies

Although the FT-IR and Raman spectroscopic techniques are excellent for the studying of surface acidity and Mo-Mo bonds, it was not possible to locate the Mo=O stretching vibration in the 940 cm^{-1} region of the IR spectra of both catalysts because Al_2O_3 exhibits a strong Al-O vibration in the same region which obscures that of the molybdenum-oxygen. Furthermore, the low concentration (0.2-1%) of Mo on the support and the high fluorescence of both catalysts renders the observation of Mo-O and Mo-Mo vibrations in the Raman spectra of both catalysts not possible.

4.1.2 Surface Acidity

The surface acidities of the catalysts K-4 and K-8, prepared by the reaction of $\text{Mo}(\pi\text{-C}_3\text{H}_5)_4$ or $\text{Mo}_2(\pi\text{-C}_3\text{H}_5)_4$ with the hydroxyl groups on $\gamma\text{-Al}_2\text{O}_3$ respectively, are shown in Table 3.1. Since the allyl ligands in both complexes behave formally as monoanions (basic nature), $\text{Mo}(\pi\text{-C}_3\text{H}_5)_4$ and $\text{Mo}_2(\pi\text{-C}_3\text{H}_5)_4$ react preferentially with the acidic groups of the inorganic support surfaces. The stronger the protonic (Brønsted) acidity of surface OH groups and the greater the number of OH groups, the more rapidly the fixing reaction proceeded. Therefore, it is not surprising to observe the complete absence of any Brønsted acidic sites from the surfaces of the catalysts after the adsorption/desorption process of pyridine and water. Only Lewis acid sites are observed on the surfaces of these catalysts.

4.1.3 Preparation of the Allyl Catalysts

The preparation of these catalysts is very difficult, expensive, and time consuming. Practically, it takes at least one week (1 week = 50-60 h of work) to prepare enough allylmagnesium chloride to synthesise about 1 g of

one of the complexes, two weeks to synthesise the monomeric, $\text{Mo}(\pi\text{-C}_3\text{H}_5)_4$ and the dimeric, $\text{Mo}_2(\pi\text{-C}_3\text{H}_5)_4$ complexes, one week to anchor them on the inorganic oxide support, and a further week for their oxidation/reduction treatment. Moreover, it needs 2-3 weeks to study their spectroscopic properties using FT-IR and Raman spectrophotometers. In conclusion, if everything goes extremely well (which is not always the case), it requires 7-8 weeks to prepare and reasonably characterize these two catalysts.

4.1.4 Problems Encountered in the Preparation of the Allyl Catalysts

We would like to mention a few problems that we have encountered during the preparation of the anchored molybdenum allyl catalysts.

(a) The reaction temperatures are crucial in these kind of reactions. In one case, we carried out the synthesis of allylmagnesium chloride at -20°C instead of -15°C , which slowed down the reaction rate between $\text{C}_3\text{H}_5\text{Cl}$ and Mg dramatically. After 12 h, the reaction mixture had to be slowly warmed up to room temperature, the exothermic reaction proceeded so fast that it produced a large volume of gases and evaporated the solvent (diethyl ether) resulting in a minor explosion. When the reaction was carried out at a temperature higher than -10°C , a very poor yield of the Grignard was obtained due to the dimerization of allyl chloride to form biallyl (1,5-hexadiene).

(b) In the preparation of the dimer, a stoichiometric quantity of the reactants (i.e. 4 moles Grignard and 2 moles MoCl_5) did not give the green dimeric product, rather it gave a red-brown product which we chose not to characterize at this stage of our experimental work. To obtain the green dimeric product, an excess of the Grignard, ca. 6:1 molar ratio, should be used.

(c) The Grignard, allyl complexes, and the catalysts obtained from them are extremely air and moisture sensitive.

(d) The yields of both molybdenum allyl complexes are small (25%).

4.2 Molybdenum Cluster Catalysts

Although the methods of the preparation of the cluster compounds described in the experimental section have already been reported in the literature, some of them required major modification to obtain multigram yields of products.

The preparation of the cluster compound $\text{Mo}_4\text{S}_4(\text{Et}_2\text{dtc})_6$, (Et_2dtc = diethyldithiocarbamate anion) is simple and straightforward. The previous synthetic procedure (142) was modified. The complex was prepared by a one pot preparation. The purification of the air and light sensitive intermediate (210) was eliminated and the final yield was increased from 25-30% to 50%. The compound was obtained as a toluene adduct. It is insoluble in water and in most cold non-chlorinated organic solvents. However, it is moderately soluble in chlorinated hydrocarbons, from which it may be crystallized out with two molecules of the solvent.

The tetranuclear complexes with the cubane-like Mo_4S_4 cluster core vary in their d-electron counts depending on the ligands and/or the oxidation state(s) of the metal atoms. The cluster Mo_4S_4 in $\text{Mo}_4\text{S}_4(\text{Et}_2\text{dtc})_6$ is two-electrons (one electron pair; i.e. a ten d-electron species) deficient of being able to saturate the six metal-to-metal bonds, whereas the same cluster in $[\text{Mo}_4\text{S}_4(\text{edta})_2]^{3-}$ (141), (edta = ethylenediaminetetraacetic acid), and $[\text{Mo}_4\text{S}_4(\text{NCS})_{12}]^{7-}$ (127) is one-electron short (eleven d-electron species).

In addition, the Mo_4S_4 cluster in $[\text{Mo}_4\text{S}_4(\text{CN})_{12}]^{8-}$ (137) is electron-precise (twelve d-electron species).

On the other hand, the complex $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9] \cdot 3\text{KCN} \cdot 4\text{H}_2\text{O}$ (86,97,101) could easily be impregnated on alumina by the virtue of its very high solubility in water. The above detailed procedure (see Experimental) to prepare this cluster compound is easy, straightforward and yields a product in the range of 60-80% of the amount of molybdenum used. This trinuclear species is of the electron-precise type. It contains the exact number of cluster d-electrons (six) necessary to form three Mo-Mo bonds. This is a general phenomenon in all compounds containing triangular trimolybdenum clusters so far reported.

Other compounds containing the cluster cores Mo_3S_4 and Mo_4S_4 were prepared from $\text{Mo}(\text{CO})_6$, Na_2S and acetic anhydride followed by a cation-exchange treatment (99,126). However, this method necessitates the use of large volumes of solvents to elute small yields of the products from a Dowex-50 WX2 cation exchange column (H-form, 25 cm long and 5.4 cm diameter). In addition, after eluting the second compound, $\text{Mo}_4\text{S}_4(\text{aq})$, with 4-5 molar HCl , the column was left black. Treatment with acid and/or base failed to regenerate and clean the expensive cation exchange resin which was then discarded. Treatment of $\text{Mo}_4\text{S}_4(\text{aq})$ with SCN^- or CN^- gave insoluble products which are not useful for catalytic studies.

The important infrared bands of the above cluster complexes are given in Table 3.2. Tentative assignments are made by comparison with literature. Spectra of compounds I, II, IV and V are reported for the first time, whereas only the Mo-S bands were previously reported for compound VII (86).

Table 3.3 shows the electronic spectra of compounds I-VII. The similarity of the spectra recorded in the solid state and in solution indicates that the cluster units in each complex persist in solution. Comparison of these solid state spectra with those of the supported clusters verifies that, in most cases, the integrity of the cluster is preserved. This result is also supported by the infrared spectral studies.

The existence of a metal-to-metal bond in a cluster compound may be detected, *inter alia*, by Raman spectroscopy, provided the compound is photochemically stable and a reasonable Raman scatterer; that is, its colour is not very dark. Unfortunately, the majority of molybdenum cluster compounds prepared to date are extremely dark in colour. Accordingly, we were able to record the Raman spectra of only two complexes (Table 3.4). Hence we doubt that Raman spectroscopy would be very useful in this project. It might be of great importance if light coloured compounds were selected.

The differential scanning calorimetric studies were undertaken to determine the actual decomposition temperature of the pure compounds and their catalysts. This may help in choosing the proper drying temperature of the catalysts after impregnation and selecting the optimum activation and reaction temperatures of the catalysts. Table 3.5 exhibits the peak positions in °C of the thermal transformations recorded under nitrogen atmosphere and their probable causes.

The cluster compounds selected as precursors to prepare supported metal-cluster catalysts are divided into three categories containing: (a) triangular metal clusters; (b) tetranuclear cubane-like clusters; and (c) hexanuclear octahedral clusters. The cluster cores in all these complexes are "electron-poor", this term designating those clusters in which the number of

metal-atom valence electrons is less or exactly equal to the number required to form a single bond between the adjacent pairs of metal atoms. The total number of electrons and the mean Mo-Mo distances within each cluster core are mentioned in Table 4.1.

Since these clusters are bonded to different ligands, no general trend of their properties could be derived. However, after supporting the cluster compounds on alumina, oxidation (with pure oxygen gas) or reduction (with hydrogen gas) to give the highest or the lowest oxidation states of the metal ions in the prepared catalysts, respectively, may lead to supported molybdenum cluster catalysts of varied nuclearity ranging from three to six, and possibly higher. Consequently, the catalytic activity may then be arranged according to their nuclearity.

4.2.1 Infrared Spectroscopy

The similarity of the infrared spectra of compounds 4, 6 and 7 before and after impregnating them on $\gamma\text{-Al}_2\text{O}_3$ (Figures 3.4,3.5; 3.8,3.9; 3.10,3.11) indicates that the cluster compounds are still intact after adsorption on the support. The spectrum of Cat-1 prepared by impregnating compound 1 on the support is very similar to that of compound 2 suggesting a transformation of complex 1 into compound 2 upon impregnation onto $\gamma\text{-Al}_2\text{O}_3$. Because compound 1 is easily hydrolysed to compound 2 in dilute mineral acid medium (94), the above transformation was probably catalysed by the acid sites on the support. The transformation of the cluster $\text{Pt}_3(\mu\text{-CO})_3(\text{PPh}_3)_4$ into $\text{Pt}_5(\mu\text{-CO})_5(\text{CO})\text{-}(\text{PPh}_3)_4$ upon impregnation onto a variety of inorganic supports has been reported (217). Due to the fact that compound 5 exhibits no bands (other than NH_4^+ and H_2O) in the region between 1000 cm^{-1} to 2700 cm^{-1} and the loss

Table 4.1. Number of Cluster Electrons
and Mean Mo-Mo Distances.

Compound	Number of Electrons	Mean Mo-Mo Distance (Å)	Reference
I	48	Not Determined	
II	48	2.788	
III	88	2.610	
IV	42	2.486	
V	42	2.505	
VI	58	2.818	
VII	42	2.773	

of the NH band on impregnating using acid medium, it is not possible to use IR spectroscopy to study its structure on the support after impregnation. However, electronic spectroscopy proved to be valuable in this case. The IR spectrum of Cat-3 was difficult to record because the only band that might be observed in the supported compound appears below 400 cm^{-1} , therefore we have to again rely on the electronic spectroscopy to study its surface structure.

4.2.2 Electronic Spectroscopy

The solid state and solution spectra of both compounds 1 and 2 are very similar (see Table 3.3). This is not surprising simply because the metal atoms in both compounds exhibit the same oxidation states (+4), their cluster cores are isoelectronic (each possess 48 electrons) and they contain the same ligand (the acetate ion). However, their electronic spectra are also similar to that of Cat-1. Taking these results in conjunction with the IR spectral study, it indicates that impregnation of compound 1 on $\gamma\text{-Al}_2\text{O}_3$ transforms it into supported compound 2 (Table 3.6). The visible spectra of Cat-3, Cat-4, Cat-5, Cat-6 and Cat-7 are similar to those of their precursor compounds (see Tables 3.3 and 3.6). These results support the conclusion drawn from the IR study and suggest that the selected molybdenum cluster compounds retain their structures on supporting them on $\gamma\text{-Al}_2\text{O}_3$ with the exception of compound 1 which transformed into supported compound 2. However, extensive decomposition of compound 5 on impregnation to give MoO_3 cannot be ruled out completely. Therefore, other surface analytical techniques such as photoelectron spectroscopy (XPS) might be extremely important tools to overcome the above problem.

4.2.3 Thermal Stability Study

Table 3.5 shows that the decomposition peaks of compounds 1-7 appear at 234, 207, 202, 377, 447, 361 and 309°C. However, the actual decompositions start well below that and gradually proceed to the peaks. The thermal decompositions of Cat-1, Cat-4, Cat-6 and Cat-7 monitored by IR spectroscopy start just above 127, 200, 250 and 150°C respectively. Whereas those of Cat-3 and Cat-5 monitored by electronic spectroscopy commence just above 200°C for both compounds (Table 3.7). Therefore the maximum testing temperatures of these catalyst should not exceed 100, 200, 200, 200, 250 and 150°C respectively, unless it is desired to change their chemical form.

4.3 Pillared Montmorillonite

4.3.1 Montmorillonite

The fact that the montmorillonite minerals occur in extremely small particles renders the single-crystal X-ray structural analysis impossible. Therefore structural information must be obtained from powder diffraction experiments. Accordingly there is considerable uncertainty regarding the detailed structure of montmorillonite. However, the generally accepted structure is that originally suggested by Hofmann, Endell and Wilm in 1933 (211) and modified by Marshall (212), Maedgefran and Hofmann (213) and Hendricks (214) as shown in Figure 4.1. According to the above concept, montmorillonite is composed of units made of two silica tetrahedral sheets with a central alumina octahedral sheet. All the tips of the tetrahedra point in the same direction and toward the center of the unit. The tetra-

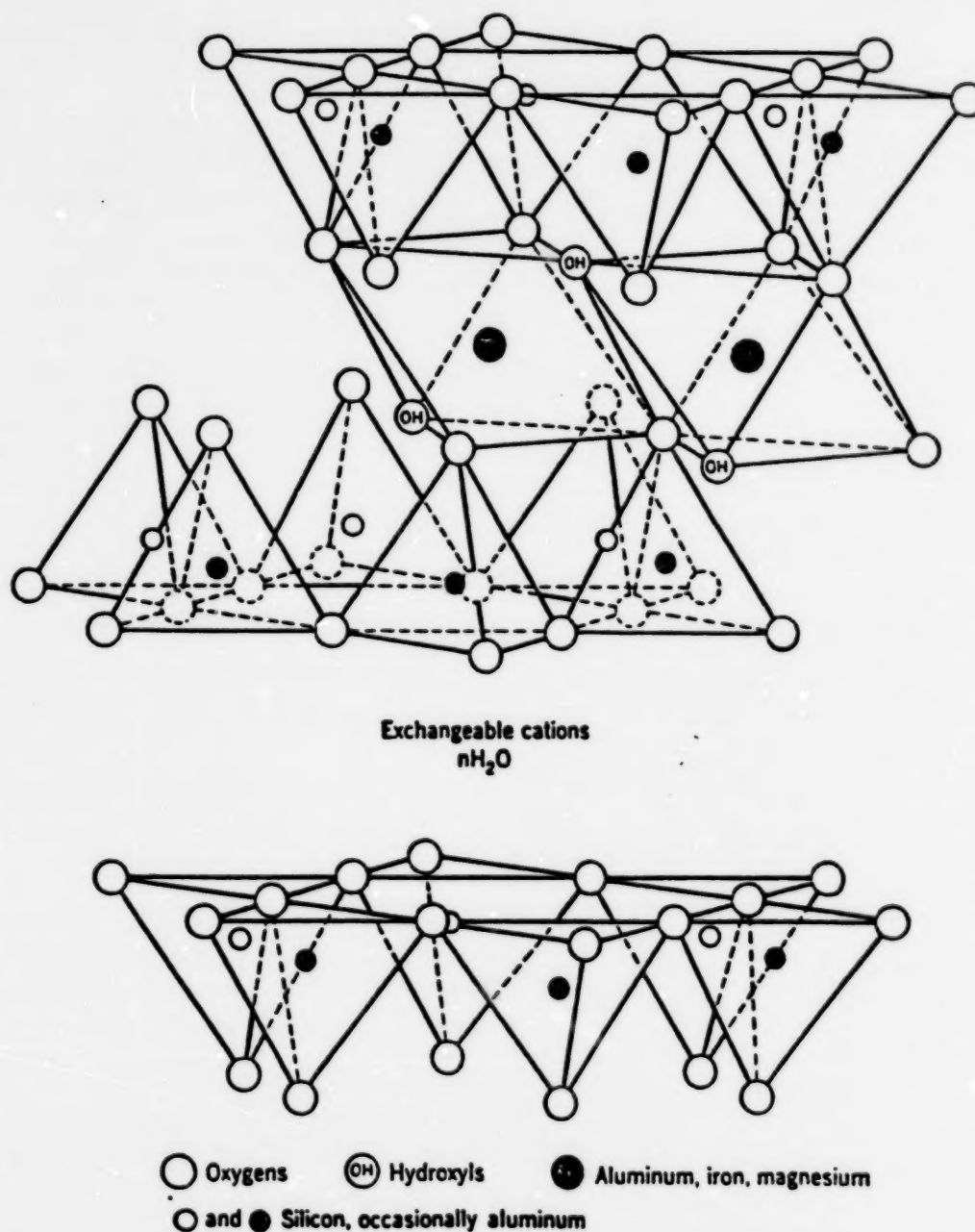


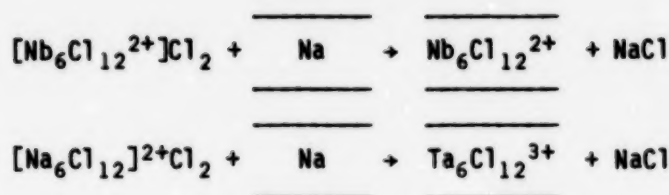
Figure 4.1. Diagrammatic sketch of the structure of montmorillonite, according to Hofmann, Endell and Wilm (211); Marshall (212); and Hendricks (214).

hedral and octahedral sheets are combined such that the tips of the tetrahedra of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms common to both tetrahedral and octahedral layers become oxygens instead of hydroxyl. The layers are continuous in the a and b directions and are stacked one above the other in the c direction.

There is a large body of literature dealing with swelling, clay-organic reactions (215) and clay-polymer complexes (216).

4.3.2 Intercalation of $M_6Cl_{12}^{2+,3+}$ (M = Nb, Ta) into Montmorillonite

The cluster compounds $M_6Cl_{12}^{2+}$ and $M_6Cl_{12}^{3+}$ (M = Nb and Ta) and their respective pillared montmorillonite were characterized by infrared and electronic spectroscopy. The infrared spectra of $Nb_6Cl_{12}^{2+}$ and $Ta_6Cl_{12}^{2+}$ exhibits bands at 348 cm^{-1} and 324 cm^{-1} respectively with one shoulder at 336 cm^{-1} that appears on the former and two at 338 cm^{-1} and 310 cm^{-1} on the latter. The electronic spectra shown in Table 3.8, indicate that dissolution of these cluster compounds does not change their spectra suggesting that they retain their structure in solution. $Ta_6Cl_{12}^{2+}$ compound is relatively stable, however it may easily be oxidized to $Ta_6Cl_{12}^{3+}$ with a few drops of 30% H_2O_2 . Conversely, $Nb_6Cl_{12}^{2+}$ can not be easily oxidized to $Nb_6Cl_{12}^{3+}$ and if left overnight with few drops of H_2O_2 it oxidizes to Nb_2O_5 . Nevertheless, comparing the spectra of $M_6Cl_{12}^{2+}$, $M_6Cl_{12}^{3+}$ (M = Nb and Ta) and their pillared clays, suggests that intercalation of $Nb_6Cl_{12}^{2+}$ into the layered structure of montmorillonite retain the electronic structure and the oxidation state intact whereas intercalation of $Ta_6Cl_{12}^{2+}$ leads to the oxidation of the cluster to $Ta_6Cl_{12}^{3+}$ as follows:



The niobium case is similar to the literature results (201) whereas the tantalum one is different, since the literature report suggested the intercalation of $\text{Ta}_6\text{Cl}_{12}^{2+}$ and not $\text{Ta}_6\text{Cl}_{12}^{3+}$. These results were expected because the work was conducted in air with an attempt to minimize the air contact and due to the ease of oxidation of $\text{Ta}_6\text{Cl}_{12}^{2+}$.

4.4 Evaluation of the Supported Mo-Cluster Compounds

4.4.1 Cumene Hydrocracking

Table 3.9 shows the activities and product distributions of some conventional molybdenum catalysts (KJ and MRF series), supported molybdenum cluster compounds (Cat-series), and fluorided supported molybdenum cluster catalysts.

On the basis of the nuclearity of the molybdenum cluster core in each precursor compound, the Cat-(1-7) series can be divided into three groups (section 4.2): (a) a catalyst containing the trinuclear triangular cluster core (Mo_3) with three Mo-to-Mo bonds; (b) one containing the tetranuclear cuboidal cluster core with six Mo-to-Mo bonds; and (c) those containing hexanuclear octahedral clusters with twelve Mo-to-Mo bonds. The activity trend through the groups is: group 3 >> group 2 >> group 1 (Cat-1 and Cat-4). The activity of Cat-5 is much higher than those of Cat-1 and Cat-4 due to the fact that it contains nine fluoride atoms coordinated to the cluster core (Mo_3). In this catalyst, the atomic ratio of the intrinsic fluoride aluminum

is one fluoride atom per ten aluminum atoms which is similar to MRF-1 and Cat-32. The increasing activity of a catalyst on fluoridation is a well known phenomenon (202-205). However, fluoriding Cat-3 and Cat-6 increases their activity by a factor of about six, from 11.5 to 65.5 and 1.6% to 9.3% respectively. Now assuming the activity of each catalyst in the Cat-(1-7) series increases by the same factor, we would expect after fluoridation the activities of Cat-1, Cat-4 and Cat-6 would increase to 7.8%, 6% and 9.6% respectively, which is still very low compared to fluorided Cat-3.

The sequence of impregnation is important, it is evident that fluoridation of Cat-3 prior to impregnation with molybdenum compound produces a more active catalyst (activity = 72.3) than fluoridation after impregnation with Mo compound (activity 65.5) which is in excellent agreement with Boorman et al. results (203). Apparently, the presence of Co in the molybdenum catalysts, whether as a conventional Co-Mo/Al₂O₃ catalyst or as in the Cat-3 series, has an opposite effect to the fluoridation. It decreases the hydrocracking activity as the activity of the cobalt-free catalysts MRF-1, Cat-3 and Cat-32 are 37.5, 11.5 and 72.3 respectively, compared to 36.0, 8.5 and 65.0 for the cobalt containing catalysts MRF-2, Cat-31 and Cat-33. However, the cobalt effect is not very clear for catalyst KJ-2 due to its very low activity.

Table 3.9 also shows that the activity increase from group 1 to group 2 is very small compared to that from group 2 to group 3. This might be attributed to the poisoning of group 2 catalyst by a nitrogen compound resulting from the nitrogen containing ligand after activation. For this reason, Cat-7 was not evaluated for this reaction.

However, comparing the catalyst prepared from the cluster compound precursors (Cat-(1-7) series) to the conventional ones obtained from ammonium

molybdate hexahydrate (KJ-1 and KJ-3) or from the anchored molybdenum allyl precursors (K-4 and K-8) we have noticed that group 1 and 2 from the Cat-(1-7) series are comparable in activity and product distribution to the conventional and molybdenum allyl catalysts. In all cases α -methylstyrene was produced in a high percentage. In contrast, Cat-3 is almost six times superior to both. In addition, the product distribution is also different, since a high percentage of styrene was produced and not α -methyl styrene. In all cases, benzene is the predominant product of hydrocracking.

4.4.2 Thiophene Hydrogenolysis (Hydrodesulfurization HDS)

The catalytic activity of Cat-(1-7) series grouped as in section 4.1 follows the following trend: group 3 >> group 1 >> group 2 with the exception of Cat-7 which has a very low activity compared to the rest of group 2. Again, the lack of activity of Cat-7 may be attributed to the poisoning of the catalyst by some nitrogen compounds obtained from the ligand. However, the activity of group 1 is comparable to that of the conventional catalyst KJ-3 which contains the same percentage of molybdenum and to KJ-1 in which the molybdenum concentration is 10%. The activities of group 2 and Cat-7 are again much lower than those of the traditional catalysts (KJ-3 and KJ-1) which is attributable to the poisoning by the nitrogen atoms in the ligands of the precursor compounds. The catalysts obtained from anchoring $\text{Mo}(\pi\text{-C}_3\text{H}_6)_4$ and $\text{Mo}_2(\pi\text{-C}_3\text{H}_6)_4$ on $\gamma\text{-Al}_2\text{O}_3$ exhibit very low activities, which is probably due to the low concentration of molybdenum in each catalyst. However, Cat-3 (group 3) shows a superb activity compared to all known molybdenum catalysts. The same catalyst shows excellent cumene hydrocracking ability (section 4.1). However the effect of cobalt addition is exactly

opposite to that observed during the hydrocracking reaction (compare Cat-3 and Cat-32 with Cat-31 and Cat-33), that is, it enhances the HDS function.

The variation of catalyst activity with time on stream differed from one catalyst to another. Generally, however, there was a drop in activity over the first 60 minutes followed by a period of relatively constant conversion percentages. In every case we have cited the values after 240 minutes for the purpose of comparing catalysts. Table 4.3 gives initial and final percentage conversions. The possible influence of coking on the catalyst performance was examined by carrying out elemental analyses on the used catalysts Cat-3, 31, 32 and 33, subsequent to HDS reactions. The fluorided catalysts Cat-32 and Cat-33 clearly were subject to more coking than their unfluorided analogues. This is consistent with their observed decreases in activity over the course of the HDS run (Table 4.3). The increase in activity of catalyst Cat-31 over the four hour run was unexpected, and may reflect ongoing sulphiding over this time period.

4.4.3 Hydrogenation of Propylene

Table 4.4 indicates that whether the activation temperature is low or high (23-500°C), the conventional as well as the supported molybdenum cluster catalysts are inactive in the hydrogenation of propylene at low temperature (23°C). Activation of Cat-3 at intermediate temperature (150-200°C) does not improve the activity of the catalyst even if the reactions are carried out at intermediate temperature. All catalysts activated at 500°C show certain hydrogenation activities, those of supported molybdenum cluster catalysts are inferior to those of the conventional catalyst. This may be explained by incomplete hydrogenation of the catalyst during the activation process due to the stabilization of the complexes by the ligands.

Table 4.2. Elemental Analysis of Used Catalysts.

Catalyst	C%	H%	C/H
Cat-3	0.44	0.22	2.0
Cat-31	0.59	0.21	2.8
Cat-32	1.18	0.06	19.7
Cat-33	1.14	0.14	8.1

Table 4.3. Activity Decrease During Catalyst Evaluation.

(a) Non-Fluorided Catalysts

Catalyst	% Conversion					
	Cumene Hydrocracking		Thiophene Hydrodesulfurization		Propylene Hydrogenation	
	Beginning of Reaction	End of Reaction	Beginning of Reaction	End of Reaction	Beginning of Reaction	End of Reaction
$\gamma\text{-Al}_2\text{O}_3$	1.4	0.9	2.9	1.3	0.5	0.5
KJ-1	2.2	2.2	18.6	8.9	78.1	78.0
KJ-2	2.7	2.4	37.9	30.3	-	-
KJ-3	-	-	11.2	6.2	76.5	76.0
K-4	1.1	1.0	3.5	1.3	-	-
K-8	1.1	1.0	3.5	1.4	-	-
Cat-1	1.2	1.3	10.5	5.1	30.8	30.5
Cat-3	15.1	11.5	17.9	10.0	32.3	18.4
Cat-4	1.0	1.0	4.5	3.1	10.3	8.9
Cat-6	1.7	1.6	2.9	1.0	7.8	6.1
Cat-7	-	-	1.8	0.9	2.4	2.4
Nb-1	-	-	1.8	0.8	-	-
Ta-1	-	-	1.3	1.0	-	-
Cat-31	11.1	8.5	37.3	42.0	45.5	25.2

(b) Fluorided Catalysts

Cat-3F	68.2	65.5	-	-	-	-
Cat-6F	7.5	9.3	-	-	-	-
Cat-32	72.7	72.3	39.5	16.5	9.3	6.7
Cat-33	66.4	65.0	42.8	17.0	10.1	10.6
Cat-5	10.5	10.3	10.8	5.1	23.6	21.8
MRF-1	39.5	37.5	25.0	8.9	-	-
MRF-2	34.3	36.0	26.6	14.3	-	-

Table 4.4. Hydrogenation of Propylene.

No.	Catalyst	Activation Temperature °C	Reaction Temperature °C	Conv. %		Remarks
				Beginning	Stabilization	
1.	$\gamma\text{-Al}_2\text{O}_3$	500	400	0.5	0.5	
2.	KJ-1	500	400	78.0	78.0	
3.	KJ-3	500	400	76.0	76.0	
4.		500	23	0.0	0.0	
5.	Cat-1	23	23	0.0	0.0	
6.		500	400	30.3	30.5	
7.	Cat-3	23	23	0.0	0.0	
8.		150	150	2.0	0.0	
9.		200	23	0.0	0.0	
10.		200	200	2.0	0.0	
11.		500	23	0.0	0.0	
12.		500	400	32.6	18.4	
13.		500	400	45.0	30.0	partial ox.
14.		500	400	56.0	40.0	partial ox.
15.	Cat-4	500	400	10.3	8.9	
16.	Cat-5	500	400	23.6	21.8	
17.	Cat-6	500	400	7.3	6.1	
18.		500	400	2.4	2.4	
19.	Cat-31	500	250	86.0	12.0	
20.		500	400	45.0	25.2	
21.	Cat-32	500	400	9.3	6.7	
22.	Cat-33	500	400	10.1	10.6	

Table 4.5. Elemental Analysis of Cat-3 and Cat-31 After Reactions.

Catalyst	Activation Temperature °C	Reaction Temperature °C	C%	H%	C/H
Cat-3	200	23	0.17	0.62	0.27
	500	400	0.20	0.24	0.83
Cat-31	500	250	0.36	0.43	0.83
	500	400	0.13	0.35	0.37

The early decreases in the activity of the catalysts are due to coking which was proved by elemental analysis (see Table 4.4). However, after activation of Cat-31 at 500°C, the reaction temperature has a dramatic effect on coke formation (Table 4.5) as during the reaction at 250°C the activity dropped from 82.0% to 12.0%.

It is evident that when the catalysts evaluations are carried out under identical conditions, the fluoride additives decrease the hydrogenation activity and facilitate coke formation whereas the addition of cobalt increases the activity with no apparent effect on coke formation.

4.4.4 Hydrotreatment of Syncrude Coker Gas Oil, SCGO

Many oil hydroprocessing studies have been reported in the literature. It is difficult to directly compare between the results of these experiments due to the large variety of oil feedstock used, catalyst type tested, reactor designs and hydrotreatment conditions applied. However, Table 3.10 compares the results of the hydrotreatment of SCGO under similar conditions using a conventional $\gamma\text{-Al}_2\text{O}_3/\text{MoO}_3/\text{CoO}$ catalyst prepared according to the existing industrial procedures and those prepared from $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$ with or without cobalt or fluoride. Although product distribution has not been determined yet, apparently the results of SCGO hydrotreatment using Cat-31 compare favourably with those obtained using the best existing catalyst, MB-481. However, the product obtained using Cat-31 had a remarkably low aromaticity (0.18). The molybdenum loading is also significantly lower than for the conventional catalysts.

The discrepancy between the calculated and found values may be attributed to the adsorption of the compounds in the glass surface of the beakers during the catalyst preparation.

Table 4.6. Elemental Analysis of Cat- Series.

Catalyst	Mo		Al	
	Found	Calculated	Found	Calculated
Cat-1	2.98	4.51	48.5 53.5	45.7
Cat-3	3.6	4.38	49.6	48.0
Cat-4	3.45	4.15	47.4	44.9
Cat-5	4.32	4.56	50.8	47.2
Cat-6	3.99	4.17	49.1	44.3
Cat-7	3.13	4.21	41.8	44.3

4.5 Catalysis by Pillared Clays

Although niobium sulfide, NbS_2 , has been reported to exhibit hydrodesulfurization properties (71) in converting dibenzenethiophene to biphenyl and cyclohexylbenzene, our evaluation of the intercalated Nb or Ta cluster cations into montmorillonite showed that they hydrodesulfurize only 0.8% and 1.0% of thiophene respectively. These poor conversions might be attributed to the very low loading of the metal (see Table 3.11). However, more in this field is necessary to increase the metal concentration into the clay and to determine the actual active sites on these surfaces. Also, the Brønsted and Lewis acidity might be determined by adsorption techniques.

Chapter 5

Conclusions and Suggestions for Future Work

The survey of the potential catalytic activity of clusters of the Group VB and VIB metals was, of necessity, restricted in its scope. Of the six metals which could have been examined only one, molybdenum, was studied in any depth. Although Nb_6 and Ta_6 clusters were used to synthesise pillared clays they were not prepared on γ -alumina or fluorided γ -alumina supports, which were the materials used successfully for the Mo_6 clusters. Future projects could be designed to cover these gaps in the study.

The application of supported Mo_6 clusters was clearly the highlight of this project. As can be seen from Tables 3.9 and 3.10 catalysts based on the precursor $(\text{H}_3\text{O}^+)_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$ had a remarkably high activity in several reactions. This was especially noteworthy in the light of the relatively low loading of molybdenum on the support. The addition of cobalt to the system, as in Cat-31 gave rise to enhanced activity in thiophene HDS studies and in propene hydrogenation. Fluoride addition clearly enhanced the hydrocracking function, while it suppressed activity in hydrogenation and HDS reactions. In hydrocracking of Syncrude Coker Gas Oil we observed very good performance from the fluorided, cobalt-containing catalyst Cat-33. If reproducible, the aromaticity reduction in the liquid product could be of great interest.

In response to the above results we attempted to extend the study of the Cat-3 series by examining:

- (a) Effect of changes in the loading of Mo_6 clusters on the surface of $\gamma\text{-Al}_2\text{O}_3$ and fluorided $\gamma\text{-Al}_2\text{O}_3$.
- (b) The use of nickel, instead of cobalt, as a promoter.

Dr. Jasim prepared such a series of materials, but in doing so he changed the preparative procedure in a significant way. To solubilize the Mo_6 cluster compounds he used aqueous HCl . The materials so formed had

vastly reduced catalytic activity. This invalidated any comparison with the catalysts described herein, and there was insufficient time left to repeat the preparations and tests.

This would clearly be a priority in any extension to the project.

Another area of need is to extend the study to include W_6 clusters and to change the chloride ligands to bromide. Indeed, an extensive study of all available M_6 clusters might be desirable. The procedures for adding fluoride, cobalt or the M_6 clusters themselves may not yet be optimal, and a thorough study would include a review of these.

With respect to the hydrotreatment of gas oils there was no attempt to optimize the parameters for these experiments. Hence the procedures for catalyst preconditioning, sulphiding, the temperature and the hydrogen pressure should all be optimized. The possibility of applying the catalysts to hydrotreating other feedstocks could also be explored.

Although the results of testing the Nb_6/Ta_6 pillared clays were disappointing it might have been due to the low concentration of the clusters in these materials. No attempt was made to support Nb_6Cl_{14} or Ta_6Cl_{14} on $\gamma-Al_2O_3$ nor to intercalate Mo_6Cl_{12} into montmorillonite. All these possible combinations of clusters and support material could be studied.

Hence the project represents little more than a preliminary survey at this stage. Nevertheless, considering the highly speculative nature of the original proposal we believe that good progress was made, and that the project was justified by the results.

References

1. J.M. Thomas and W.J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis", Academic Press Inc. (London) 1967, p. 1.
2. E.L. Muetterties and M.J. Krause, *Angew. Chem. Int. Ed. Engl.* 22 (1983) 135.
3. A. Nakamura and M. Tsutsui, "Principles and Applications of Homogeneous Catalysis", John Wiley and Sons, Inc., 1980, p. 9.
4. J. Falbe and H. Bahrmann, *J. Chem. Ed.* 61 (1984) 961.
5. B.F.G. Johnson, Ed., "Transition Metal Clusters", John Wiley and Sons Ltd., 1980, p. 545.
6. N.Y. Topsoe and H. Topsoe, *J. Catal.* 84 (1983) 386.
7. C.P. Li and D.M. Hercules, *J. Phys. Chem.* 88 (1984) 456.
8. T.G. Parham and R.P. Merrill, *J. Catal.* 85 (1984) 295.
9. C. Wivel, B.S. Clausen, R. Candia, S. Morap and H. Topsoe, *J. Catal.* 88 (1984) 497.
10. J.C. Bailar, *Catal. Rev. Sci. Eng.* 10 (1974) 17.
11. J. Manansen, in "Catalysis, Heterogeneous and Homogeneous", Eds., B. Delmon and G. Jannes, Elsevier, Amsterdam, 1975, p. 293.
12. G. Jannes, *Ibid.*, p. 83.
13. J. Manansen, *Platinum Metals Rev.* 15 (1971) 142.
14. M.S. Scurrall, *Ibid.* 21 (1977) 92.
15. K.G. Allum, R.D. Hancock, I.V. Howell, R.C. Pitkethly and P.J. Robinson, *J. Organomet. Chem.* 87 (1975) 187.
16. K.G. Allum, R.D. Hancock, S. McKenzie and R.C. Pitkethly in "Catalysis", Ed., J.W. Hightower, *Proc. 5th Int. Cong. Catal.* North Holland Pub., Amsterdam, 1973, Vol. 1, p. 477.

17. N. Kohler and F. Dawans, *Rev. Inst. Fr. Petrole Ann. Combust. Liquides* 27 (1972) 105.
18. W.O. Haag and D.D. Whitehurst, Reference 16, p. 465.
19. Z.M. Michalska and D.E. Webster, *Platinum Metals Rev.* 18 (1974) 65.
20. K.G. Allum, R.D. Hancock, I.V. Howell, S. McKenzie, R.C. Pitkethly and P.J. Robinson, *J. Organomet. Chem.* 87 (1975) 203.
21. K. Marcinkowska, L. Rodrigo, S. Kaliagnine and P.C. Roberge, *J. Mol. Catal.* 33 (1985) 189.
22. A. Kinting, H. Krause and M. Capka, *J. Mol. Catal.* 33 (1985) 215.
23. D.C. Bailey and S.H. Langer, *Chem. Rev.* 81 (1981) 109.
24. J. Phillips and J.A. Dumesic, *Appl. Catal.* 9 (1984) 1.
25. Yu. I. Yermakov, *Catal. Rev.* 13 (1976) 77 and references therein.
26. Y. Iwasawa, Y. Nakano and S. Ogasawara, *J. Chem. Soc., Faraday Trans.* 74 (1978) 2968.
27. Y. Iwasawa and S. Ogasawara, *Ibid.* 75 (1979) 1465.
28. Y. Iwasawa, H. Kubo, M. Yamagishi and S. Ogasawara, *Chem. Soc. Jpn., Chem. Lett.* (1980) 1165.
29. Y. Iwasawa, T. Nakamura, K. Takamatsu and S. Ogasawara, *J. Chem. Soc., Faraday Trans.* 76 (1980) 939.
30. Y. Iwasawa, M. Yamagishi and S. Ogasawara, *J. Chem. Soc., Chem. Commun.* (1980) 871.
31. Y. Iwasawa, H. Ichinose and S. Ogasawara, *J. Chem. Soc., Faraday Trans. I* 77 (1981) 1763.
32. Y. Iwasawa, Y. Sato and H. Kuroda, *J. Catal.* 82 (1983) 289.
33. Y. Iwasawa and M. Yamagishi, *J. Catal.* 82 (1983) 373.
34. Y. Iwasawa, Y. Sasaki and S. Ogasawara, *J. Chem. Soc., Chem. Commun.* (1981) 140.

35. Y. Iwasawa and S. Ogasawara, Chem. Soc. Jpn., Chem. Lett. (1980) 127.
36. J. Manassen, "Heterogeneous Catalysis", in "Catalysis Progress in Research", Eds., F. Basolo and R.L. Burwell, Jr., Plenum Press, New York, 1973, p. 177.
37. L.L. Murrell, "Immobilization of Transition Metals: Complex Catalysts on Inorganic Supports", in "Advanced Materials in Catalysis", Materials Science Series, Academic Press, New York, 1977, p. 235.
38. R.D. Hancock, I.V. Howell, R.C. Pitkethly and P.J. Robinson, Reference 11, p. 293.
39. T.O. Michell and D.D. Whitehurst, U.S. Patent No. 3 980 583 (1976).
40. S.L. Davidova and N.A. Plate, Coord. Chem. Rev. 16 (1975) 195.
41. S. Bhaduri and K.R. Sharma, J. Chem. Soc., Dalton Trans. (1984) 2309.
42. A.T. Jurewicz, L.D. Rollman and D.D. Whitehurst, "Homogeneous Catalysis II", Adv. Chem. Series 132, Eds., D. Forster and J.F. Roth, Am. Chem. Soc. (1974) 240.
43. L.D. Rollman, Inorg. Chim. Acta 6 (1972) 137.
44. J.P. Candlin and H. Thomas, Reference 42, p. 212.
45. L.J. Boucher, A.A. Oswald and L.L. Murell, "Olefin Hydroformulation Catalysts with Rhodium or Cobalt Phosphine Complexes Covalently Anchored to Silica", Preprints, Petroleum Div., Am. Chem. Soc. Meeting, Los Angeles, Calif., March 1974, p. 162.
46. B.C. Gates and J. Lieto, Chemtech. (1980) 195.
47. J.L. Graff, R.D. Sanner and M.S. Wrighton, J. Am. Chem. Soc. 101 (1979) 273.
48. G.D. Mercer, J.S. Shu, T.B. Rauchfuss and D.M. Roundhill, J. Am. Chem. Soc. 97 (1975) 1967.

49. C.U. Pittman, Jr., R.C. Ryan, J. McGee and J.P. O'Conner, J. Organomet. Chem. 178 (1979) C43.
50. V.W. Day, R.O. Day, J.S. Kristoff, F.J. Hirsekorn and E.L. Muettertides, J. Am. Chem. Soc. 97 (1975) 2571.
51. R.M. Laine, R.G. Rinker and P.C. Ford, J. Am. Chem. Soc. 99 (1977) 252.
52. F. L'Eplattenier, P. Matthys and F. Calderazzo, Inorg. Chem. 9 (1970) 342.
53. K. Cann, T. Cole, W. Slegeir and R. Pettit, J. Am. Chem. Soc. 100 (1978) 3969.
54. J.L. Vidal, Z.C. Mester and W. Walker, U.S. Patent No. 4 115 428 (1978), Union Carbide.
55. J.S. Bradley, J. Am. Chem. Soc. 101 (1979) 7419.
56. M.G. Thomas, B.F. Beier and E.L. Muettertides, J. Am. Chem. Soc. 98 (1976) 1296.
57. R.M. Laine, J. Am. Chem. Soc. 100 (1978) 645; Ann. N.Y. Acad. Sci. 133 (1980) 124.
58. I. Kojima, E. Miyazaki, Y. Inoue and I. Yasumori, J. Catal. 59 (1979) 427.
59. E.I. Ko, J.M. Hupp, F.H. Rogan and W.J. Wagner, J. Catal. 84 (1983) 85.
60. T. Iizuka, K. Ogasawara and K. Tanabe, Bull. Chem. Soc. Jpn. 56 (1983) 2927.
61. K. Ogasawara, T. Iizuka and K. Tanabe, Chem. Soc. Jpn., Chem. Lett. (1984) 645.
62. C.J. Wright and W.A. England, Niobium, Proc. Int. Symp. 1981, Ed., H. Stuart, Metall. Soc. A.I.M.E. Warrendale, Pub., 1984, p. 561.
63. R. Parathasarathy and J.G. Giapetta, France Patent No. 1 555 139 (1968).

64. T. Shirasaki, K. Moriya and I. Furuoya, Japan Patent No. 76-143615 (1976).
65. Y. Oda, K. Uchid and T. Morimoto, Japan Patent No. 73-49715 (1973).
66. Y. Nanba, T. Suzuki, Y. Nakanishi and Y. Okuda, Japan Patent No. 75-39292 (1975).
67. J.F. McMahon, France Patent No. 1 500 632 (1966).
68. R.C. Hansford, U.S. Patent No. 3 480 684 (1969).
69. L. Bajars, U.S. Patent Nos. 3 291 854 (1966); 3 308 196 (1967); 3 308 200 (1967).
70. T.H. Johnson, U.S. Patent No. 4 480 049 (1984).
71. R.R. Chianelli, T.A. Pecoraro and M.B. Dines, Ger. Patent No. 2 821 289 (1978).
72. D.M. Haynes and W.C.E. Higginson, J. Chem. Soc., Dalton Trans. (1976) 309.
73. V.A. Likholobov, V.A. Semekolenov, B.L. Moroz and Yu. I. Yermakov, "Fixed Polynuclear Complexes as New Prospective Catalysts", Russ. Prog. V. Khim. Tekhnol., Novosibirsk (1984) 164. CA: 102:095074P.
74. Yu. I. Yermakov, L.N. Arzamaskova and V.L. Kuznetsov, "Clusters in Heterogeneous Catalysis", Russ., Koord. Khim. 10 (1984) 877. CA: 101 98342g.
75. M. Dorbon, Rev. Inst. Fr. Petrole 39 (1984) 497.
76. G. Collier, D.J. Hunt, S.D. Jackson, R.B. Moyes, I.A. Pickering, P.W. Wells, A.F. Simpson and R. Whyman, J. Catal. 80 (1983) 154.
77. Ibid. 86 (1984) 333; 86 (1984) 342.
78. Y. Doi, H. Miyake, A. Yokota and K. Soga, Inorg. Chim. Acta 105 (1985) 69.
79. H. Hayashi and J.B. Moffat, J. Catal. 77 (1982) 473.

80. T. Yamaguchi, A. Mitoh and K. Tanabe, Chem. Soc. Jpn., Chem. Lett. (1982) 1229.
81. S.M. Kulikov and I.V. Kozhenikov, Kinet. Katal. 24 (1983) 42.
82. (a) E.L. Mueterties, C and EN, Aug. 30 (1982) 28.
(b) F. Bottomley and F. Grein, Inorg. Chem. 21 (1982) 4170.
83. D.J. Darensbourg and D.J. Zalewski, Organometall. 3 (1984) 1598.
84. A. Müller, R. Jostes and F.A. Cotton, Angew. Chem. Int. Ed. Engl. 19 (1980) 875 and references therein.
85. Y. Jiang, A. Tang, R. Hoffman, J. Huang and J. Lu, Organometall. 4 (1985) 27 and references therein.
86. A. Müller and U. Reinsch, Angew. Chem. Int. Ed. Engl. 19 (1980) 72.
87. R.B. King, D.M. Braitsch and P.N. Kapoor, J. Am. Chem. Soc. 97 (1975) 60.
88. M.R. Churchill and S.W.Y. Chang, J. Chem. Soc., Chem. Commun. (1974) 248.
89. S.Z. Goldberg, B. Spivack, G. Stanley, R. Eisenberg, D.M. Braitsch, J.S. Miller and M. Abkowitz, J. Am. Chem. Soc. 99 (1977) 110.
90. A. Bino, Inorg. Chem. 21 (1982) 1917.
91. F.A. Cotton, S.A. Duraj and W.J. Roth, J. Am. Chem. Soc. 106 (1984) 3527.
92. A. Simon and H.G.V. Schnering, J. Less Commun. Metals 11 (1966) 31.
93. H. Schafer and H.G.V. Schnering, Angew. Chem. 76 (1967) 833.
94. A. Birnbaum, F.A. Cotton, Z. Dori, D.O. Marler, G.M. Reisner, W. Schwetzer and M. Shaia, Inorg. Chem. 22 (1983) 2723.
95. A. Bino, F.A. Cotton, Z. Dori, S. Koch, H. Küppers, M. Miller and J.C. Sekutowski, Inorg. Chem. 17 (1978) 3245.

96. F.A. Cotton, Z. Dori, D.O. Marler and W. Schwotzer, *Inorg. Chem.* 23 (1984) 4033.
97. A. Müller, R. Jostes, E. Eltzner, C-S. Nie, E. Diemann, H. Bögge, M. Zimmermann, M. Dartmann, U. Reinsch-Vogell, S. Che, S.J. Cyvin and B.N. Cyvin, *Inorg. Chem.* 24 (1985) 2872.
98. H. Keck, W. Kuchen, J. Mathow, B. Meyer, D. Mootz and H. Wunderlich, *Angew. Chem. Int. Nat. Ed. Engl.* 20 (1981) 975.
99. T. Shibahara and H. Kuroa, *Abs. 5th Int. Conf. Chem. and Uses of Molybdenum*, Newcastle-Upon-Tyne, England, July 1985, p. 59.
100. T. Shibahara, H. Hattovi and H. Kuroa, *J. Am. Chem. Soc.* 106 (1984) 2710.
101. N.C. Howlader, G.P. Haight, Jr., J.W. Hambley, G.A. Lawrance, K.M. Rahmoeller and M.R. Snow, *Aust. J. Chem.* 36 (1983) 377.
102. W-H. Pan, M.E. Leonowicz and E.I. Stiefel, *Inorg. Chem.* 22 (1983) 672.
103. A. Bino, F.A. Cotton and Z. Dori, *J. Am. Chem. Soc.* 100 (1978) 5252.
104. *Ibid.* 101 (1979) 3842.
105. S.F. Gheller, T. Hambley, R.T.C. Brownlee, M.J. O'Connor, M.R. Snow and A.J. Wedd, *J. Am. Chem. Soc.* 105 (1983) 1527.
106. S.P. Cramer, P.K. Eidem, M.T. Paffett, Z. Dori and H.B. Gray, *J. Am. Chem. Soc.* 105 (1983) 799.
107. M.T. Paffett and F.C. Anson, *Inorg. Chem.* 22 (1983) 1347.
108. E.O. Fischer and F. Röhrscheid, *J. Organomet. Chem.* 6 (1966) 53.
109. E.W. Golbersuch and R.C. Young, *J. Am. Chem. Soc.* 71 (1949) 2402.
110. P.J. Vergamini, H. Vahrenkamp and L.F. Dahl, *J. Am. Chem. Soc.* 93 (1971) 6327.

111. J. Marcoll, A. Rabenau, D. Mootz and H. Wundelich, *Rev. Chim. Miner.* 11 (1974) 607.
112. A. Müller, R.G. Bhattacharyya, W. Eltzner, N. Mahon, A. Neumann and S. Sarkar, *Proc. 3rd Int. Conf. Chem. and Uses of Molybdenum, Climax Molybdenum Comp., Ann. Arbor, 1979*, p. 59.
113. A. Bino, M. Ardon, I. Maor, M. Kaftory and Z. Dori, *J. Am. Chem. Soc.* 98 (1976) 7093 (formula revised, see Reference 117).
114. M.D. Curtis and W.M. Butler, *J. Chem. Soc. Chem. Comm.* (1980) 998.
115. H. Keck, W. Kuchen, J. Mathow and H. Wunderlich, *Angew. Chem. Int. Ed. Engl.* 21 (1982) 929.
116. H.S. Harned, C. Pauling and R.B. Corey, *J. Am. Chem. Soc.* 82 (1960) 4815.
117. *Ibid.* 103 (1981) 243.
118. M. Ardon, A. Bino, F.A. Cotton, Z. Dori, M. Kaftory, B.W.S. Kolthammer, M. Kapon and G. Reisner, *Inorg. Chem.* 20 (1981) 4083.
119. M. Ardon, A. Bino, F.A. Cotton, Z. Dori, M. Kaftory and G. Reisner, *Inorg. Chem.* 21 (1982) 1912.
120. A. Bino and D. Gibson, *J. Am. Chem. Soc.* 104 (1982) 4383.
121. A. Müller, A. Ruck, M. Dartmann and U. Reinsch-Vogell, *Angew. Chem. Int. Ed. Engl.* 20 (1981) 483.
122. T.H. Halbert, K. McGavley, W.-H. Pan, R.S. Czernuszewicz and E.I. Stiefel, *J. Am. Chem. Soc.* 106 (1984) 1849.
123. F.A. Cotton, Z. Dori, D.O. Marler and W. Schwotzer, *Inorg. Chem.* 23 (1984) 4033.
124. K. Mennemann and R. Mattes, *Angew. Chem. Int. Ed. Engl.* 15 (1976) 118.

125. M. Ardon, F.A. Cotton, Z. Dori, A. Fang, M. Kapon, G.M. Reisner and M. Shaia, J. Am. Chem. Soc. 104 (1982) 5395.
126. (a) F.A. Cotton, Z. Dori, Roas Liusar and W. Schwotzer, J. Am. Chem. Soc. 107 (1985) 6734.
(b) F.A. Cotton, M.P. Diebold, Z. Dori, R. Liusar and W. Schwotzer, J. Am. Chem. Soc. 107 (1985) 6735.
127. P. Kathirgamanathan, M. Martinez and A.G.J. Sykes, J. Chem. Soc., Chem. Comm. (1985) 953.
128. M.H. Chisholm, J.C. Huffman and R.L. Kelly, J. Am. Chem. Soc. 101 (1979) 7100.
129. R. Mattes and K. Mühlisepen, Z. Naturforschung B 35b (1980) 265.
130. M.H. Chisholm, D.L. Clark and J.C. Huffman, Polyhedron 4 (1985) 1203.
131. T.R. Ryan and R.E. McCarley, Inorg. Chem. 21 (1982) 2072.
131. (a) W.W. Beers and R.E. McCarley, Inorg. Chem. 24 (1985) 468.
(b) R.E. McCarley, T.R. Ryan and C.C. Toradi, ACS Symp. Ser. No. 155 (1981) 41.
132. (a) E.O. Fischer and K. Ulm, K. Ulm Dissertation, Universität München, 1961.
(b) W. Chen, L.Y. Goh and T.C.W. Mak, Organometallics 5 (1986) 1997.
133. L.F. Dahl, Lecture Presented at the VIth Int. Conf. on Organometallic Chem., Amherst, 1973.
134. A.W. Edelblut, K. Folting, J.C. Huffman and R.A.D. Wentworth, J. Am. Chem. Soc. 103 (1981) 1927.
135. A. Müller, W. Eltzner, H. Bögge and S. Sarkar, Angew. Chem. Int. Ed. Engl. 21 (1982) 535.

136. A. Müller, W. Eltzner, W. Clegg and G.M. Sheldrick, *Angew. Chem. Int. Ed. Engl.* 21 (1982) 536.
137. A. Müller, W. Eltzner, H. Bögge and R. Jostes, *Angew. Chem. Int. Ed. Engl.* 21 (1982) 795.
138. H. Keck, W. Kuchen and J. Mathow, *Inorg. Chim. Acta* 83 (1984) L31.
139. J.A. Bandy, C.E. Davies, J.C. Green, M.L.H. Green, K. Prout and D.P.S. Rogers, *J. Chem. Soc., Chem. Comm.* (1983) 1395.
140. K.L. Wall, K. Folting, J.C. Huffman and R.A.D. Wentworth, *Inorg. Chem.* 22 (1983) 2366.
141. T. Shibahala, H. Kuroya, K. Matsumoto and S. Ooi, *J. Am. Chem. Soc.* 106 (1984) 789.
142. T.C.W. Mak, K.S. Jasim and C. Chieh, *Inorg. Chem.* 24 (1985) 1587.
143. A.W. Edelblutt and R.A.D. Wentworth, *Inorg. Chem.* 19 (1980) 1110.
144. C. Chieh, K.S. Jasim and D. Nash, unpublished results.
145. H. Schäfer and H.G.V. Schnering, *Angew. Chem.* 76 (1964) 833.
146. L.R. Bateman, J.F. Blount and L.F. Dahl, *J. Am. Chem. Soc.* 88 (1966) 1082.
147. R. Siepmann, H.G.V. Schnering and H. Schäfer, *Angew. Chem. Int. Ed. Engl.* 6 (1967) 637.
148. P.A. Vaughan, J.H. Sturdivant and L. Pauling, *J. Am. Chem. Soc.* 72 (1950) 5477.
149. D.D. Klenworth and R.A. Walton, *Inorg. Chem.* 20 (1981) 1151.
150. F.W. Koknat, J.A. Parson and A. Vongvusharintra, *Inorg. Chem.* 13 (1974) 1699.
151. A. Simon, *Z. Anorg. Allg. Chem.* 355 (1967) 311.
152. D. Imoto and J.D. Corbett, *Inorg. Chem.* 19 (1980) 1242.

153. J. Sola, Y. Do, J.M. Berg and R. Holm, *Inorg. Chem.* 24 (1985) 1706.
154. J.L. Meyer and R.E. McCarley, *Inorg. Chem.* 17 (1978) 1867.
155. S.A. Best and R.A. Walton, *Inorg. Chem.* 18 (1979) 484.
156. R.A. Walton, *Prog. Inorg. Chem.* 16 (1972) 1.
157. J.E. Fergusson, *Prep. Inorg. React.* 7 (1971) 93.
158. A.D. Hamer, T.J. Smith and R.A. Walton, *Inorg. Chem.* 15 (1976) 1014.
159. D.L. Kepert, R.E. Marshall and D. Taylor, *J. Chem. Soc., Dalton Trans.* (1974) 506.
160. J.C. Sheldon, *J. Chem. Soc.* (1962) 410.
161. R.D. Hogue and R.E. McCarley, *Inorg. Chem.* 9 (1970) 1354.
162. J.E. Fergusson, B.H. Robinson and C.J. Wilkins, *J. Chem. Soc. (A)* (1967) 486.
163. P. Nannelli and B.P. Block, *Inorg. Chem.* 7 (1968) 2423.
164. K.S. Jasim, C. Chieh and T.C.W. Mak, *J. Cryst. Spect. Res.* 15 (1985) 403.
165. A. Birnbaum, F.A. Cotton, Z. Dori and M. Kapon, *Inorg. Chem.* 23 (1984) 1617.
166. A. Bino, F.A. Cotton and Z. Dori, *Inorg. Chim. Acta* 33 (1979) L133.
167. M.H. Chisholm, D.M. Hoffman and J.C. Huffman, *Inorg. Chem.* 24 (1985) 796.
168. P.J. Kuhn and R.E. McCarley, *Inorg. Chem.* 41 (1965) 1482.
169. R.M. Barrer and D.M. MacLeod, *Trans. Faraday Soc.* 51 (1955) 1290.
170. R.M. Barrer and J.S.S. Reay, *Trans. Faraday Soc.* 53 (1957) 1253.
171. R.M. Barrer, "Zeolites and Clay Minerals as Sorbents and Molecular Sieves", Academic Press, New York/London, 1978.
172. M.M. Mortland and V. Berkheiser, *Clays Clay Miner.* 24 (1976) 60.

173. J. Shabtai, N. Frydman and R. Lazar, in "Proceedings, 6th Intern. Congress on Catalysis", London 135 (1976) 1, Eds. G.C. Bond, P.B. Wells and F.C. Tompkins, The Chem. Soc., London, 1977, p. 660.
174. R.H. Leoppert, M.M. Mortland and T.J. Pinnavaia, Clays Clay Miner. 27 (1979) 201.
175. G.W. Brindley and R.E. Samples, Clays Clay Miner. 12 (1977) 229.
176. N. Lahav, U. Shani and J. Shabtai, Clays Clay Miner. 26 (1978) 107.
177. S. Yamanaka and G.W. Brindley, Clays Clay Miner. 27 (1979) 119.
178. M.L. Occelli and R.M. Tindwa, Clays Clay Miner. 31 (1983) 22.
179. R.J. Lussier, J.S. Magee and D.E.W. Vaughan, Preprints, 7th Canadian Symposium Catalysis, Edmonton, Alberta, 180, pp. 88-95.
180. R. Burch and C.I. Warburton, J. Catal. 97 (1986) 503.
181. T. Endo, M.M. Mortland and T.J. Pinnavaia, Clays Clay Miner. 28 (1980) 105.
182. T. Endo, M.M. Mortland and T.J. Pinnavaia, Clays Clay Miner. 29 (1981) 153.
183. S.P. Christiano, W. Jialiang and T.J. Pinnavaia, Inorg. Chem. 24 (1985) 1222.
184. P.M. Boorman, R.A. Kydd, Z. Sarbak and A. Somogyvari, J. Catalysis 96 (1985) 115.
185. G. Wilke, B. Bogdanović, P. Hardt, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Water and H. Zimmermann, Angew. Chem. Int. Edn. Engl. 5 (1966) 151.
186. F.A. Cotton and J.R. Pipal, J. Am. Chem. Soc. 93 (1971) 5441.
187. O. Grummitt, E.P. Budewitz and C.C. Chudd, "Organic Synthesis", Collect. Wiley, New York, N.Y., 1963, Vol. 4, p. 749.

188. O. Grummitt, E.P. Budewitz and C.C. Chudd, "Inorganic Synthesis", Wiley, New York, N.Y., 1972, Vol. 13, p. 74.
189. Yu. I. Yermakov, B.N. Kuznetsov and Yu. A. Ryndin, J. Catalysis 42 (1976) 73; Yu. I. Yermakov and B.N. Kuznetsov, Prep. 2nd Japan-Soviet Catalysis Seminar, Tokyo, 1973, p. 65.
190. J.P. Candlin and H. Thomas, Adv. Chem. Ser. 132 (1974) 212.
191. W.L. Jolly, "The Synthesis and Characterization of Inorganic Compounds", Prentice-Hall, Inc., Englewood Cliffs, N.J., 1970, pp. 456-459.
192. K.R. Rodgers, R.K. Murmann, E.O. Schlemper and M.E. Shelton, Inorg. Chem. 24 (1985) 1313.
193. Z. Dori and G. Wilkinson, Inorg. Syn. 13 (1972) 87.
194. J.V. Brencic and F.A. Cotton, Inorg. Syn. 13 (1972) 170.
195. G.D. Thorn, "The Dithiocarbamates and Related Compounds", 2nd Ed., Elsevier, New York, 1962.
196. (a) A. Müller, S. Sarkar, R.G. Bhattacharyya, S. Pohl and M. Dartmann, Angew. Chem. Int. Ed. Engl. 17 (1978) 535.
(b) A. Müller, S. Pohl, M. Dartmann, J.P. Cohen, J.M. Bennet and R.M. Kirchner, Z. Naturforsch. B34 (1979) 434 [X-ray structure analysis].
(c) A. Müller, R.G. Bhattacharyya and B. Pfefferkorn, Chem. Ber. 112 (1979) 778 [very simple synthesis].
197. D. Adams, "Metal-Ligand and Related Vibrations", Edward Arnold (Publishers) Ltd., London, 1967.
198. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", John Wiley and Sons, New York, 1978.
199. L.J. Bellamy, "The Infrared Spectra of Complex Molecules", 3rd Ed., Chapman and Hall, London, Vol. 1, 1975.

200. G. Socrates, "Infrared Characteristic Group Frequencies", A. Wiley-Interscience Publishing, 1980.
201. S.P. Christiano, J. Wang and T.J. Pinnavaia, *Inorg.* 24 (1985) 1222.
202. P.M. Boorman, J.F. Kriz, J.R. Brown and M. Ternan, in "Proceedings, 8th International Congress in Catalysis", Berlin, 1984, Vol. II, p. 281.
203. P.M. Boorman, J.F. Kriz, J.R. Brown and M. Ternan, in "Proceedings, 4th Climax International Conference Chemistry and Uses of Molybdenum", Eds. H.F. Barry and P.C.H. Mitchell, (1982), pp. 192-196.
204. P.M. Boorman, R.A. Kydd, Z. Sarbak and A. Somogyvari, *J. Catalysis* 96 (1985) 115.
205. Z. Sarbak, P.M. Boorman, R.A. Kydd and R. Somogyvari, *Stud. Surf. Sci. Catal.* 19, (1984) 55.
206. Y. Iwasawa, T. Chiba and N. Ito, *J. Catalysis* 99 (1986) 95.
207. Y. Iwasawa and N. Ito, *J. Catalysis* 96 (1985) 613.
208. K. Marcinkowska, S. Kaliaguine and P.C. Roberge, *J. Catalysis* 90 (1984) 49.
209. G.H. Ballard, *Adv. Catalysis* 23 (1973) 263.
210. D.A. Brown, W.K. Glass and K.S. Jasim, *Chem. Uses Molybdenum, Proc. Int. Conf., 4th Ed.*, 156 (1982).
211. U. Hofmann, K. Endell and D. Wilm, *Z. Krist.* 86 340 (1933).
212. C.E. Marshall, *Z. Krist.* 91 (1935) 433.
213. E. Maedghefranz and U. Hofmann, *Z. Krist.* 98 (1937) 299.
214. S.B. Hendricks, *J. Geol.* 50 (1942) 276.
215. B.K.G. Theng, "The Chemistry of Clay-Organic Reactions", John Wiley and Sons, New York, Toronto, 1974.
216. B.K.G. Theng, "Formation and Properties of Clay-Polymer Complexes", Elsevier, 1979.

217. R. Bender and P. Braunstein, *J. Chem. Soc., Chem. Commun.*, (1983) 334.
218. (a) A.J. Leffler and R. Penque, *Inorg. Synth.* 12 (1970) 186.
- (b) A.D. Beveridge and H.C. Clark, *Halogen Chemistry*, Ed. V. Gutmann, Academic Press, London, 3 (1967) 179.
- (c) F.W. Koknat, J.A. Parsons and A. Vongvusharintra, *Inorg. Chem.* 13 (1974) 1699.